

AMERICAN CHEMICAL JOURNAL.

ON THE DECOMPOSITION OF DIAZO COMPOUNDS.
IX.—ON THE REACTION OF ETHYL AND METHYL ALCOHOLS
WITH PARADIAZOMETATOLUENESULPHONIC ACID IN THE
PRESENCE OF VARIOUS SUBSTANCES.¹

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Introduction.

Since it became known that the statement of Griess to the effect that, when diazo compounds are boiled with alcohol the decomposition products are nitrogen, aldehyde, and a substance formed by the replacement of the diazo group by hydrogen, does not hold good for all cases, but that in some cases the ethoxy group, and not hydrogen, enters into the compound, various efforts have been made to determine the conditions that decide which of these two reactions, known as the alkoxy and hydrogen reactions respectively, will take place. Work has been done in this laboratory on the influence of pressure and temperature on the reaction, and it has been shown that increase of pressure and simplicity of the alcohol radical favor the alkoxy reaction.

Metcalf,² in studying the reaction of certain alcohols with

¹ From the Author's Thesis, submitted to the Board of University Studies of the Johns Hopkins University for the degree of Doctor of Philosophy, June, 1895. The work was undertaken at the suggestion of Professor Remsen, and carried on under his supervision.

² This JOURNAL, 15, 301.

paradiazometatoluenesulphonic acid, showed that when the diazo compound is decomposed in alcohol, both the alkoxy and hydrogen reactions take place, the former greatly predominating, though the ratio changes somewhat with varying conditions of temperature and pressure. A few years later Beeson,¹ in his investigations on the action of certain diazo compounds on methyl and ethyl alcohols, carried on in this laboratory, having discovered the fact that the presence of an excess of alkalies and of some other substances induced the hydrogen reaction, it was thought desirable to study similar reactions in the case of paradiazometatoluenesulphonic acid.

Preparation of Paradiazometatoluenesulphonic Acid.

As a starting point the paratoluidinemetasulphonic acid of commerce was taken. This was a light brown powder, slightly soluble in cold, readily soluble in boiling water. After boiling with animal charcoal, two, or at most three, recrystallizations gave a pure white product, that separated from the solution in prismatic needles. By adding a little hydrochloric acid with the animal charcoal to the boiling solution the first crystallization gave a nearly white product.

Von Pechmann,² who obtained paratoluidinemetasulphonic acid by treating paratoluidine with fuming sulphuric acid, describes the product as of a sulphur yellow color which it was impossible to remove, and Metcalf,³ who followed the same method of preparation, speaks of the difficulty of obtaining the acid in a pure white condition.

The pure white paradiazometatoluenesulphonic acid thus obtained was finely pulverized and diazotized by suspending it in alcohol of 92 per cent. and treating it with a strong current of nitrous fumes, produced by the action of nitric acid on arsenious oxide, in the manner described by Metcalf, and with substantially the same results.

100 grams of the acid were suspended in 30 cc. of alcohol, and the nitrous fumes passed through the emulsion for thirty minutes. The action was very slow at first, but soon increased as the mixture warmed up. The alcohol took on an orange color which deepened to a dark brownish red shade. The

¹ This JOURNAL, 16, 235.

² Ann. Chem. (Liebig), 173, 195.

³ This JOURNAL, 15, 301.

diazo compound was of a light pink tint, and settled readily to the bottom of the flask after shaking, while, on the other hand, the alcohol with the suspended acid would remain milky for some time. This rapid settling to the bottom was taken as indicative of the completion of the reaction. The diazo compound was filtered off by means of a filter-pump, washed with a small quantity of alcohol and some ether and then dried. The yield in this and subsequent experiments, approached closely to the theoretical amount, never falling below 95 per cent. Some of the diazo compound dissolved in the alcohol and, on standing, crystallized out. The compound when dry keeps for months in the dark, but exposed to the light it slowly turns yellow. It is very stable, and small portions have been ground in a mortar without exploding.

Decomposition of Paradiazometatoluenesulphonic Acid in Methyl Alcohol in Presence of Various Substances.

1. *In Presence of Sodium Methylate.*—In 80 cc. of pure methyl alcohol, redistilled over lime, 5 grams of metallic sodium were dissolved. The solution of sodium methylate was then placed in a beaker in a freezing-mixture, and when its temperature fell below zero, the paradiazometatoluenesulphonic acid was added, small portions at a time. There was immediate action, a gentle evolution of gas took place, the diazo compound gradually disappeared, and the alcohol took on a straw yellow color. After the addition of a few small portions, the temperature rose to 5° and the color deepened. No further addition of the diazo compound was made until the thermometer had again fallen below zero, and the temperature was kept below that point throughout the experiment. When about half the diazo compound had been added, an orange-yellow powder began to settle in the bottom of the beaker. The addition of the diazo compound was continued until 25 grams had been added; the beaker was then removed from the freezing-mixture and left to stand over night. During the decomposition, a slightly irritating odor, other than that of the alcohol, could be observed. When the reaction had ceased the material was poured into an evaporating-dish, and the methyl alcohol driven off by heating on a water-bath.

The substance readily dried. When nearly dry, some volatile product, having a very irritating odor, and acting upon the eyes to produce an immediate flow of tears, began to be given off. The hard light-brown substance which remained in the dish was pulverized, and rubbed in a mortar, with its own weight (30 grams) of phosphorus pentachloride. The reaction was immediate and violent, and fumes of phosphorus oxychloride were given off. There remained behind a black viscid oil, together with a quantity of tarry products. This was poured into water, and a dark brown oil settled in the bottom of the vessel. Placed for some time in a test-tube, in a freezing-mixture, the oil did not solidify. The oil was washed with water several times and finally treated with strong ammonia, with which it readily reacted, going into solution and heating up considerably. Excess of ammonia was expelled by evaporating to dryness on a water-bath, and the residue extracted several times with ether. On distilling off the ether there remained behind a brown, syrupy liquid, which, on cooling, became solid and showed a crystalline structure. This was dissolved in boiling water and treated with animal charcoal and filtered. On cooling, small rhomboidal scales separated out, slightly brown in color. By several recrystallizations and treatment with animal charcoal, large clear white fern-shaped crystals were obtained which melted at 108° . This was the melting-point of the small quantity of metatoluenesulphonamide obtained by Metcalf from a mixture consisting for the greater part of paraethoxymetatoluenesulphonamide. The yield was 4.5 grams.

Another experiment was tried under similar conditions, with the exception of that of temperature, which was allowed to rise to 20° , and the results were essentially the same, with perhaps a slight increase in the tarry by-product. After the alcohol was evaporated off, a light brown color remained behind. This was heated on a water-bath until thoroughly dry. The same irritating odor was noticed. The alcohol which was distilled off was tested for aldehyde, and it responded at once to the silver-mirror test. A solution of the light brown powder was also tested for aldehyde, and its presence was indicated in the same way. By treatment with phosphorus penta-

chloride and ammonia, as in the first case, four grams of the amide were obtained. In these and the subsequent experiments, no product other than the metatoluenesulphonamide was obtained.

2. *In Presence of Sodium Carbonate.*—25 grams of the diazo acid were decomposed in 200 cc. of absolute methyl alcohol, in which 9 grams of dried sodium carbonate were suspended. When the alcohol had been cooled below zero, the addition of small portions of the diazo compound was begun. As the amount of substance added increased, the alcohol gradually took on a pink tinge, but, beyond an occasional bubble at long intervals, there was no apparent evolution of gas. The flask was then removed from the freezing-mixture, placed on a water-bath, and gently warmed to 30°, when a slow evolution of gas occurred. The flask was left standing over night. In the morning the alcohol was found to be colored brownish-red, and the sodium carbonate formed a layer at the bottom, seemingly in undiminished quantity. A thin layer of undecomposed or undissolved diazo compound covered the sodium carbonate. An occasional bubble of gas would rise through this upper layer. It was placed on a water-bath and heated to 35°, when the action became quite rapid, and continued till nearly all the sodium carbonate had disappeared. The temperature was then 46°. The flask was next connected with a condenser, and nearly all the alcohol was distilled off. The residual brown powder, dried on the water-bath, weighed 27 grams, and was darker in color than that obtained in the experiments with sodium methylate. By treating the salt in the usual way 12 grams of a light brown colored amide was obtained. A second experiment with sodium carbonate and methyl alcohol was performed, the alcohol being at the room temperature, 20°. A gentle evolution of gas began at once, and the temperature rose gradually while the diazo compound was added. It was not allowed to rise above 45°, being cooled when it reached that point by immersion in cold water. The remainder of the process was exactly as in the previous case, resulting in a like yield, 12 grams of amide.

3. *In Presence of Sodium Hydroxide.*—In this experiment, 7 grams of fused sodium hydroxide were broken up and placed

in an Erlenmeyer flask with 200 cc. of methyl alcohol. Small portions of the diazo compound were added, and the action was immediate, the temperature, which was 21° at the beginning of the experiment, rising so rapidly that the flask was placed in ice-water and kept there throughout the experiment. After 25 grams of the diazo compound had been added, the flask was left standing till all action had ceased, when the alcohol was distilled off as in the preceding cases. The yield of amide was 12 grams.

4. *In Presence of Zinc Dust.*—In a flask containing 200 cc. of absolute methyl alcohol, 10 grams of zinc dust were placed. The diazo compound was then added in small portions, the flask being well shaken after every addition. Action took place at once with a rapid rise of temperature from 17° at the beginning, to 30° . When this latter temperature was reached the flask was placed in ice-water. In this experiment the alcohol did not become discolored for a long time, whereas in the other decompositions, a very small proportion of the whole quantity of the diazo compound sufficed to give the alcohol a decided red color. When 25 grams of diazo acid had been added, the alcohol was of a light straw color.

After all action had ceased, the solution was filtered to remove the residual zinc dust. Five grams of pure white amide, melting at 108° , were obtained.

5. *In Presence of Calcium Carbonate.*—In this experiment 300 cc. of methyl alcohol and 15 grams of powdered calcium carbonate were taken. The diazo compound was added in small portions at a time, but no action was noticed. The flask was then placed on a water-bath, and heated up to 45° , but still there was no evolution of gas. Fifty grams of the diazo acid were added, and the whole left to stand over night. In the morning the calcium carbonate covered the bottom of the flask, with the lighter, undissolved diazo compound forming a layer above.

From this experiment it seems that the presence of calcium carbonate has no influence whatever on the diazo decomposition, which entirely agrees with Beeson's¹ results in his experiments with diazobenzene nitrate and calcite.

¹ This JOURNAL, 16, 235.

An excess, 17 grams of zinc dust, was then added to the mixture. Bubbles of gas formed at once, and, as the contents of the flask became heated, the reaction went on briskly. The solution, which was of a pink color, soon became colorless, and at the conclusion of the action, it had the light yellow color observed in previous experiments with zinc dust. After filtering from the calcium carbonate and residual zinc dust, drying, and proceeding as before, a yield of 10 grams of pure white amide was obtained.

Decomposition of Paradiazometatoluenesulphonic Acid in Ethyl Alcohol in Presence of Various Substances.

1. *In Presence of Sodium Ethylate.*—3.5 grams of sodium were dissolved in 20 cc. of absolute ethyl alcohol, and the solution placed in a 500 cc. Erlenmeyer flask and cooled down to 5° below zero. The diazo compound was added in small portions at a time. Each portion sank at once to the bottom of the flask, but in a few moments rose rapidly to the surface, colored dark red, and an evolution of gas began. The odor of aldehyde was very marked from the beginning. As the addition proceeded the solution thickened, and became very dark in color. The evolution of gas became sluggish and continued for a long time after all the diazo compound had been added. The temperature was kept below zero until 25 grams of the diazo compound had been added, when the flask was removed from the freezing-mixture, and the contents left to attain the room temperature.

The mixture was allowed to stand over night, then placed upon a water-bath, and the alcohol distilled off. A hard black mass remained in the flask. This could not be removed, and the alcohol was poured back into the flask and heated on the water-bath; but the mass remained hard. It was left standing two and a half days, but with no better results. The alcohol was distilled off again, and the mass dissolved readily in a small quantity of water. This solution was evaporated to dryness over a water-bath. The dried mass was powdered and weighed 35 grams. It was of a dark brown color, much darker than the corresponding compound obtained from methyl alcohol. There remained a black viscous mass. This

was shaken up with ether, the ether solution poured off, and the ether distilled off.

From this only 4 grams of dark-colored amide were obtained. The experiment was repeated with the same quantities of material, but no efforts were made to keep the temperature down. The only difference noted was in the rapidity of the reaction which, in the second experiment, was much greater than when the flask was kept in the freezing-mixture, but in neither case was it nearly as brisk as when methyl alcohol was employed. A yield of 3 grams of amide and a greater quantity of tarry matter than in the previous experiment, were obtained.

2. *In Presence of Sodium Carbonate.*—9 grams of dried sodium carbonate were suspended in 200 cc. of absolute alcohol, and, after cooling the mixture to zero, 25 grams of the diazo compound were gradually added. There was no apparent action. The flask was taken from the freezing-mixture and placed on a water-bath. When its temperature was 32° the action became brisk, but not nearly as much so as in the case of methyl alcohol and sodium carbonate. The odor of aldehyde was distinctly perceptible. The flask was kept on the water-bath till its contents attained a temperature of 50°. It was then removed, and left standing over night. In the morning the alcohol was colored a deep red, and bubbles of gas were still rising to the surface. Upon heating the flask the evolution of gas became very rapid. When this had almost entirely ceased the alcohol was distilled off. The brown mass remaining behind was removed very easily and powdered. It weighed 35 grams. From this 10 grams of pure white amide were obtained.

A second experiment was performed, the variation in this case consisting in using 90 per cent. alcohol in place of absolute alcohol. This experiment was performed at the room temperature. Upon the addition of the diazo compound there was a brisk evolution of gas, but no odor of aldehyde. The temperature of the contents of the flask rose up to above 40°. After standing a while it was heated on a water-bath to 45°, when the action proceeded briskly for some time, the sodium carbonate gradually disappearing, till but a small portion of it remained.

The odor of aldehyde was now perceptible. From this it seems that the reaction took place in two stages, the first being probably the formation of the sodium salt of paradiazometatoluenesulphonic acid, and the second the decomposition of this compound.

Proceeding as in the second experiment, 7 grams of a light brown amide were obtained.

3. *In Presence of Sodium Hydroxide.*—In this experiment an excess, 7 grams, of fused sodium hydroxide was broken up into small pieces and placed in an Erlenmeyer flask with 200 cc. of absolute ethyl alcohol. The experiment was begun at the room temperature. The reaction was similar to that with sodium ethylate, but the decomposition took place much more slowly than when methyl alcohol and sodium hydroxide were used. After distilling off the alcohol, drying and powdering, 35 grams of a brown substance were obtained. The yield of amide obtained was 10 grams, and its color was brown.

4. *In Presence of Zinc Dust.*—In this experiment 300 cc. of absolute ethyl alcohol and 17 grams of zinc dust were taken. 50 grams of the diazo compound were slowly added. No freezing-mixture was employed, but the temperature was kept down by placing the flask in running water.

The evolution of gas was a little sluggish at first, but, as the contents of the flask became warm, it became brisk. The odor of aldehyde was noticed from the very beginning. When the reaction was over the alcohol remained limpid and of a light orange color, in distinction to the dark-red, syrupy liquid which resulted from the other experiments with ethyl alcohol. The alcohol was distilled off, leaving a hard, almost white residue at the bottom of the flask. This gave 7 grams of a nearly pure white amide.

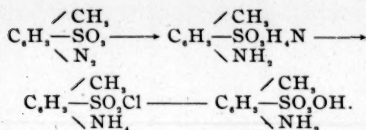
5. *In Presence of Ammonia.*—200 cc. of absolute methyl alcohol were saturated with dry ammonia gas and the solution was cooled to zero. Upon the addition of the diazo compound there was no apparent action. After waiting some time the flask was removed from the freezing-mixture and its contents were allowed to acquire the room temperature (20°), when action took place. As more diazo compound was added the temperature rose rapidly, and the flask was cooled

by placing it in a dish of cold water. Upon the completion of the reaction the alcohol was distilled off, the residue removed from the flask, dried and powdered. The powder was treated in a mortar with an equal amount of phosphorus pentachloride; the reaction was very violent; fumes of phosphorus oxychloride were given off, but in place of the appearance of an oil, the mixture in the mortar thickened and became solid. Water was added to this, upon which the mass foamed up, and after the reaction was over bunches of yellow needles appeared throughout the dark red liquid.

A quantity of crystals was removed and washed with water. They were found to be very soluble in water. Repeated boiling with animal charcoal failed to remove or lessen their yellow color. Heated up to 300° , they charred without melting. On adding hydrochloric acid to a solution of the substance, white needles, similar in appearance to the original paratoluidinemetasulphonic acid, crystallized out. It was supposed that it might be the ammonium salt of paratoluidinemetasulphonic acid, and to test this about 20 grams of it was diazotized in the usual manner, and the diazo compound, similar in appearance to that obtained heretofore, was then decomposed in absolute methyl alcohol, to which an excess of fused sodium hydroxide had been added. The decomposition took place in all respects similar to that of the diazo acid in methyl alcohol and sodium hydroxide. On drying, powdering, and treating with phosphorus pentachloride, a dark-colored oil was obtained, which was washed and treated with ammonia. The resulting amide was extracted with ether, boiled with water and animal charcoal, and brown crystals were obtained which, by repeated purifications, gave large pure white scales, of exactly the same appearance as the recrystallized amides previously obtained, and melting at the same temperature.

The experiment was repeated, using ethyl alcohol, with like results.

Hence the decomposition of paradiazometatoluenesulphonic acid in ammoniacal alcohol, must have taken place as follows:



A comparison of the different yields of purified amides was made as follows, the number representing the yield in grams of pure amide obtained from the decomposition of 100 grams of the paradiazometatoluenesulphonic acid.

	In methyl alcohol.	In ethyl alcohol.
With sodium.....	24.8	19.0
" sodium carbonate..	36.0	33.0
" sodium hydroxide..	33.0	24.0
" zinc dust.....	17.0	24.0

Each weight is the average of at least three experiments.

From these experiments it is seen that the sodium carbonate reaction yielded the largest amount of amide. The compound resulting from the decomposition of the diazo acid in presence of sodium carbonate, and which contained the excess of sodium carbonate originally added, was also the one most slowly acted upon by phosphorus pentachloride.

On the other hand, with the exception of the zinc dust reaction, all the others gave a quantity of tarry matter upon treatment with phosphorus pentachloride.

The apparent purity of the oil obtained by treating with phosphorus pentachloride the product of the decomposition of paradiazometatoluenesulphonic acid in the presence of zinc dust; the absence of all traces of tarry matter; and the large clear white crystals of amide which the very first crystallization yielded, marked the zinc reaction as by far the cleanest method of decomposition. The great disparity in the yields of amide obtained by this and the other methods of decomposition, was not, however, in its favor.

It was thought that the heat of the reaction might have decomposed or volatilized a part of the sulphonchloride formed, and experiments were made with a less violent chlorinating agent than phosphorus pentachloride. Accordingly 50 grams of the diazo compound were decomposed in 300 cc. of methyl

alcohol and 17 grams of zinc dust. After the decomposition, the solution was filtered and evaporated to dryness, 55 grams of a light-brown powder being obtained. This was added in small portions at a time, to 70 grams of phosphorus trichloride, contained in a 300-cc. round-bottomed flask. After a few grams had been added small bubbles began to appear, coming from the powder, which darkened somewhat in color, and became gummy. As the addition of substance went on, the temperature rose very slightly. After the whole had been added the flask was put aside over night.

In the morning the contents of the flask consisted of a brown gum, which covered the bottom, and an almost clear liquid on top. Most of the clear liquid, the greater part of which was phosphorus trichloride, was poured off, placed in a flask, and distilled under diminished pressure. There remained behind a small quantity of a slightly yellow oil. This was shaken up with water; it became lighter in color, diminished somewhat in quantity, and settled readily to the bottom of the flask.

The flask containing the gummy substance and the remainder of the clear liquid, was then connected with a condenser, and heated on a water-bath under diminished pressure. Some more phosphorus trichloride came over. When distillation had ceased the flask was removed, and the slightly yellow liquid above the gummy material poured into water. It settled at once to the bottom. Water was added to the flask containing the brown gum, and this dissolved slowly, giving off small globules of oil which gathered together at the bottom. The three portions of oil were put together and washed repeatedly with water.

The amide was made by pouring the oil into 150 to 200 cc. of strong ammonia, and shaking vigorously. In a few minutes the contents of the flask became warm and the oil dissolved, forming a clear, light-yellow solution. Upon cooling, large, slightly yellow crystals of the amide separated out. After filtering, the mother-liquid was evaporated to dryness and the residue extracted with ether, which resulted in a still smaller addition to the total amount of amide obtained. After boiling with

animal charcoal, the first crystallization yielded, from 100 grams of the diazo compound, 45 grams of large pure white fern-shaped crystals, which melted sharply at 108°.

The decomposition was repeated, using absolute ethyl alcohol in place of methyl alcohol. The decomposition did not take place as readily as when methyl alcohol was employed, but, upon slightly warming the alcohol, it became rapid. The alcohol remained nearly colorless throughout the experiment, while when methyl alcohol was used, it turned to an orange color. The yield of amide was a little greater than by the methyl alcohol method, 100 grams of the diazo acid giving 50 grams of pure amide.

The results obtained by heating the product of the diazo decomposition in presence of zinc dust with phosphorus trichloride, suggested a like experiment with that obtained by decomposing the diazo acid in presence of sodium carbonate.

Because the amides obtained by treating the residue, after the decomposition in presence of sodium carbonate, with phosphorus pentachloride and ammonia respectively approached that from the zinc dust reaction in whiteness and surpassed it in quantity, it was thought the substitution of the trichloride for the pentachloride of phosphorus, would lead to a larger and cleaner yield of metatoluenesulphonchloride.

Accordingly, about 25 grams of the diazo compound were decomposed in absolute ethyl alcohol in which 8 grams of dried sodium carbonate were suspended.

The reaction took place as in the like experiments previously performed, and about 30 grams of dried material were obtained. This was powdered, and added little by little, to 30 grams of phosphorus trichloride. Each small portion added settled to the bottom, and there was no appearance of change. When the whole amount was added, the powder absorbed the liquid trichloride, but the contents of the flask did not warm up, nor was any other indication of a reaction noticed. Left to stand over night, its appearance was unchanged in the morning.

The flask was next connected with a reflux-condenser, and heated on a water-bath for two hours. A portion of the moist powder was then recovered from the flask and thrown into cold

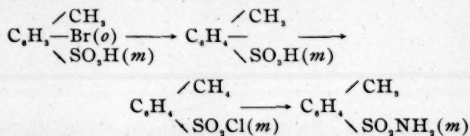
water. There was the usual reaction between phosphorus trichloride and water, but no trace of an oily sulphonchloride. The substance was therefore removed from the flask and rubbed in a mortar with 30 grams of phosphorus pentachloride, resulting in the usual quantity of liquid metatoluenesulphonchloride, which was converted into the amide.

From this experiment it was concluded that the product obtained when the diazo compound was decomposed in presence of sodium carbonate would not react with phosphorus trichloride and all subsequent yields of sulphonchloride were obtained by the zinc dust and phosphorus trichloride treatment.

Metatoluenesulphonamide.

Having on hand a quantity of pure amide, obtained as a result of the preceding experiments, its properties were carefully studied and compared with the metatoluenesulphonamides described in the literature.

The amide was first mentioned, in 1873, by Müller,¹ who made it by reducing the barium salt of orthobrommetatoluenesulphonic acid, by means of sodium amalgam, and then by the phosphorus pentachloride reaction forming the sulphonchloride, which, treated with ammonia, gave the amide. The transition from the orthobrommetatoluenesulphonic acid to the amide, he supposed took place as follows:

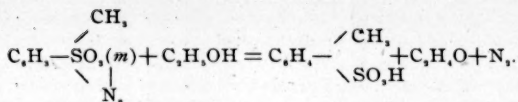


Müller describes the amide as easily soluble in ether, alcohol and ammonia, and as crystallizing from water at 40° in large scales, and from water at 20° in slender needles. Its melting-point was 90°-91°.

A year later Pechmann² obtained what he claimed to be metatoluenesulphonamide by decomposing paradiazometatoluenesulphonic acid in alcohol under pressure, according to the following equation:

¹ Ann. Chem. (Liebig), 169, 51.

² Ibid. 173, 195.



From this acid he obtained an amide, like Müller's, soluble in hot water, alcohol and ether, but which crystallized in rhombic scales and in brilliant leaves and needles, and melted "somewhere below 100°."

The amide was next obtained in 1874, by Pagel,¹ who also employed the diazo reaction, making first the diazo compound of orthotoluidinesulphonic acid, changing this into the bromtoluenesulphonic acid, removing the bromine by long-continued treatment with sodium amalgam, and then proceeding to the amide by the usual reactions. Pagel's amide was tolerably easily soluble in cold water, much more so in hot water, and easily soluble in alcohol, chloroform, and ether. From all these solvents it crystallized out in large leaves, which melted at 104°.

In 1877, Beckurts² described an amide which he obtained by fractional crystallization from a mixture of amides. But this product, and that obtained two years later by Claesson and Wallin,³ was a mixture of the para and ortho compounds, as will be shown in the second part of this thesis.

In 1879, F. H. S. Müller,⁴ by treating the metadiazotoluene salts with sulphurous acid, obtained an amide melting at 107°. This also was probably impure, for an anilide obtained from the same sulphonchloride, had a much lower melting-point than the one which will be described further on.

Neville and Winther,⁵ (1880), by heating orthodiazotoluenesulphonic acid under pressure with alcohol, and by reduction of bromtoluenesulphonic acid by means of sodium amalgam, obtained a toluenesulphonic acid, which gave, on treating its potassium salt with phosphorus pentachloride, a sulphonchloride, and an amide which melted at 106°.5-107°.5.

Chase Palmer,⁶ in 1882, repeated Hübner and Müller's process of obtaining the amide, and found a product identical

¹ Ann. Chem. (Liebig), 176, 297.

² Ber. d. chem. Ges., 10, 943.

³ Ibid., 12, 1848.

⁴ Ibid., 12, 1348.

⁵ J. Chem. Soc., 37, 628.

⁶ This JOURNAL, 4, 140.

in all its properties with that described by these investigators.

In 1886, Klason¹ prepared the amide after the method of Pechmann, and found it to have a melting-point of 108° crystallizing in monoclinic scales and octahedra.

In the same year Vallin,² admitting the evidence of the impurity of the amide obtained by himself and Klason,³ made the compound by the method of Pechmann and described it as crystallizing from water in leaves melting at 107° , and from alcohol in monoclinic crystals which melted at 108° . About this time also, Noyes and Walker⁴ made what they claimed to be the metatoluenesulphonamide by treating orthobromotoluene with fuming sulphuric acid, making the sodium salt and eliminating the bromine atom by means of zinc dust. The sodium salt was then treated with phosphorus pentachloride and the oily chloride thus obtained converted into an amide which melted at 90° - 91° .

The next contribution to our knowledge of metatoluenesulphonamide was made by Metcalf,⁵ in his work "On the Reaction of Certain Alcohols with Paradiazometatoluenesulphonic Acid," which showed that when this acid is decomposed by boiling with alcohol, both the alkoxy and the hydrogen reactions take place, the former to a much greater degree than the latter. Metcalf succeeded in separating a small quantity of the metatoluenesulphonamide from mixtures of it and paraethoxymetatoluenesulphonamide. He found for these specimens melting-points ranging between 95° and 108° .

The amide which was obtained in the experiments herein described was carefully compared with that described by the above-mentioned investigators.

The specimens resulting from the phosphorus pentachloride reaction were boiled with animal charcoal and recrystallized six times. That which resulted from the sulphonchloride obtained by the phosphorus trichloride treatment, gave pure white crystals after its first recrystallization. From concentrated solutions the amide came down in brilliant hex-

¹ Ber. d. chem. Ges., 19, 2887.

² *Ibid.*, 19, 2952.

³ *Ibid.*, 12, 1848. The names of these two investigators were written Claesson and Wallin.

⁴ This JOURNAL, 8, 186.

⁵ *Ibid.*, 15, 301.

agonal scales, and from more dilute solutions it separated out in beautiful large fern-like growths. It is soluble to a very slight extent in cold water, but easily soluble in hot water at a temperature of 70°. It is exceedingly soluble in alcohol, from which it crystallizes in large monoclinic prisms.

Analyses of the amide gave the following results :

I. 0.3020 gram of the amide gave 0.5445 gram of carbon dioxide, and 0.1472 gram water.

II. 0.3003 gram of the amide gave 0.5425 gram of carbon dioxide, and 0.1450 gram water.

III. 0.2391 gram of the amide gave 0.3302 gram of barium sulphate.

IV. 0.2910 gram of the amide gave 0.3950 gram of barium sulphate.

V. 0.2210 gram of the amide gave 0.0202 gram of nitrogen.

VI. 0.1800 gram of the amide gave 0.0149 gram of nitrogen.

VII. 0.2185 gram of the amide gave 0.0178 gram of nitrogen.

The sulphur determinations were made by Liebig's method. Nitrogen determination V. was made by the Dumas method ; VI. and VII. were made, by Wilfarth's modification of the Kjeldahl method, by Mr. J. W. Lawson, of this laboratory, who also made the carbon and hydrogen determinations.

	Calculated for $C_8H_4<\begin{smallmatrix} CH_3 \\ SO_2NH_2 \end{smallmatrix}$	I.	Found.	II.
C	49.12	49.17		49.26
H	5.26	5.40		5.36
S	18.71	18.92		18.73
N	8.18	8.15		8.28-8.15

The amide obtained by Müller¹ was described as crystallizing at 20° in slender needles. Though a great many observations were made, in no case did the amide come down in this form, but always in hexagonal scales sometimes bunched in fern-shaped leaves.

Von Pechmann's amide came down in rhombic scales and needles, and though it melted at 104°, was far from being

¹ Ann. Chem. (Liebig), 169, 51.

pure metatoluenesulphonamide, for, as shown by Metcalf's work, it contained some paraethoxymetatoluenesulphonamide. Pagel's amide differed from that herein described in being tolerably easily soluble in cold water and in crystallizing from all its solvents in large leaves. The other amides referred to above, which were prepared after the methods of Müller and von Pechmann, or a combination of both, cannot be considered as pure products.

Oxidation of Metatoluenesulphonamide.

4 40 40
3 60 10
20
An experiment was made, having for its aim the oxidation of metatoluenesulphomamide to metasulphaminebenzoic acid. To a mixture of 80 grams of concentrated sulphuric acid diluted with three times its volume of water, and 60 grams of potassium bichromate, 20 grams of metatoluenesulphonamide were added. The flask containing the mixture was connected with a reflux-condenser and heated gently over a low flame. The action began almost immediately, and became so energetic that cold water had to be added to the contents to prevent foaming over. After boiling for an hour, the oily layer of melted amide which covered the surface entirely disappeared, and the flask was removed and its contents, after cooling, were poured in cold water. A mass of crystals separated. These were filtered by means of a filter-pump, and washed with water till free from color. They were then treated on the funnel with cold sodium carbonate solution, when most of the acid dissolved. The substance which remained on the filter was examined and proved to be pure metatoluenesulphonamide. It weighed about two grams.

Metasulphaminebenzoic Acid.

The sodium salt, which passed in solution through the filter, was treated with hydrochloric acid and a quantity of minute scales separated out. These were filtered off, dried, and recrystallized. They gave a melting-point of 233° (uncorrected). From the 20 grams of metatoluenesulphonamide a yield of 12 grams of the metasulphaminebenzoic acid resulted. It was carefully compared with the metasulphaminebenzoic acid which Limpricht and Usler¹ obtained by heating together

¹ Ann. Chem. (Liebig), 106, 36.

sulphobenzamide and potassium hydroxide, and which was described as separating from cooled mixture in scales melting above 200° . This acid was further described as sparingly soluble in cold water, more easily in ether, and very soluble in alcohol. Kept in a molten state for ten minutes, it stiffened on cooling to a crystalline mass easily soluble in water. Its barium salt was made by adding barium carbonate to a boiling solution of the acid. This was easily soluble in water, from which it crystallized out in small masses resembling wavellite, and containing four molecules of water of crystallization. Its silver salt consisted of long silky needles which contained two molecules of water of crystallization and did not blacken on boiling or long exposure to the light.

A small portion of the metasulphaminebenzoic acid, made by oxidizing metatoluenesulphonamide, was gently heated upon platinum foil. It behaved like Limpricht and Uslar's acid, volatilizing, and passing off in white fumes free from the irritating effect of the fumes of benzoic acid. About one gram of the acid was heated in a test-tube in a sulphuric-acid bath to 245° – 250° for forty-five minutes. Upon cooling, it stiffened to a brown, glassy mass, which was easily soluble in cold water, from which it crystallized out, on evaporating down the solution, in long needles.

Barium Salt of Metasulphaminebenzoic Acid.—The barium salt of the acid was made by neutralizing a boiling solution of the acid by means of pure barium carbonate. The undecomposed carbonate was filtered off and the solution evaporated down. Upon standing, small radiating nodules formed like those described by Limpricht and Uslar.

The analysis of the barium salt showed its composition to be

$$\left(\text{C}_6\text{H}_4 \begin{array}{c} \text{CO}_2 \\ \text{SO}_2\text{NH}_2 \end{array} \right)_2 \text{Ba} + 4\frac{1}{2}\text{H}_2\text{O}.$$

I. 0.2345 gram of the barium salt, dried by exposure to the air, lost, upon being heated to 180° , 0.0306 gram water.

II. 0.3022 gram of the salt, gave off at 180° , 0.0394 gram water.

III. 0.2039 gram of the anhydrous barium salt, gave upon ignition with sulphuric acid, 0.0880 gram of barium sulphate.

IV. 0.2623 gram of the anhydrous salt, gave 0.1126 gram of barium sulphate.

	Calculated.	I.	Found.	II.
H ₂ O	13.10	13.05		13.03
Ba	25.51	25.37		25.24

The dehydrated salt takes up water very rapidly, which makes its weighing difficult. The difference between our results for the water of crystallization and those of Limpricht and Uslar, may be due to this, and also to the fact that their barium salt was dried over sulphuric acid, and was heated only to 110°.

Silver Salt—The silver salt was made by boiling a solution of the acid with silver carbonate. It was soluble to a slight extent in boiling, and insoluble in cold water. From hot water it crystallized out in long, fine needles, which slowly blackened upon exposure to the light. It contained no water of crystallization, and analysis showed that it corresponded to the formula $C_6H_4 \begin{smallmatrix} \diagup COOAg \\ \diagdown SO_2NH_2 \end{smallmatrix}$.

I. 0.2256 gram of the salt gave 0.0779 gram silver.

II. 0.2710 gram of the salt gave 0.0945 gram silver.

	Calculated.	I.	Found.	II.
Ag	35.06	35.52		34.90

Limpricht and Uslar found two molecules of water of crystallization in this salt.

On the whole, if we except the water of crystallization of the silver salt, there are enough points of resemblance between the salts of metasulphaminebenzoic acid obtained by the oxidation of metatoluenesulphonamide, and those of Limpricht and Uslar's compound, to indicate the identity of the two substances.

Conclusions.

From the work described in this article we may conclude that:

1. When paradiazometatoluenesulphonic acid is decomposed in alcohol in the presence of an excess of some alkalis and zinc dust, only the hydrogen reaction takes place.

2. When the decomposition takes place in alcohol saturated with ammonia, the ammonium salt of paratoluidinemeta-sulphonic acid is formed.

3. The nature of the alcohol, whether methyl or ethyl alcohol, has little, if any, influence on the reaction.

4. If we except the case of decomposition in the presence of calcium carbonate, countenance is given to the suggestion that the neutralization of free acid determines the hydrogen reaction. But why calcium carbonate acts differently has not yet been determined.

ON METATOLUENESULPHONIC ACID.

BY JOHN J. GRIFFIN.

Introduction.

The action of sulphuric acid on toluene was first investigated by Jaworsky,¹ who described one toluenesulphonic acid as the resulting compound.

In 1869, Engelhardt and Latschinoff² heated toluene with sulphuric acid, and made the potassium salt of the resulting acid. This crystallized out in two forms: prisms which were difficultly soluble, and needles which were more easily soluble in water. These two potassium salts were fused with caustic potash and gave two isomeric cresoles, the para and ortho compounds.

Barth,³ working in a similar manner, obtained, by fusing the crude mixture of potassium salts, paroxybenzoic and salicylic acids.

Anna Wolkow⁴ confirms this result, but ascribes the meta position to the sulphon group in the acid which passed over into salicylic acid, and further, made two sulphonchlorides, one liquid and one solid, and two amides, that from the α or para acid melting at 137° , and that from the β or, as it was then called, the meta acid, melting at 153° – 154° .⁵

Fittig and Ramsay,⁶ in order to settle definitely the position of the sulphon group in the acid which Anna Wolkow called

¹ Ztschr. Chem., 1, 272.

² *Ibid.*, (1869), 617.

³ Ann. Chem. (Liebig), 152, 91.

⁴ Ztschr. Chem. (1870), 321.

⁵ This was previous to V. Meyer's work on the orientation of the hydroxybenzoic acids.

⁶ Ann. Chem. (Liebig), 168, 242.

the metatoluenesulphonic acid, proceeded as follows: They treated toluene with sulphuric acid, made the isomeric potassium salts, and separated as far as possible by fractional crystallization, the para salt. The mother liquid, which contained some of the para and an isomeric salt which was either ortho or meta, was then evaporated to dryness and thoroughly mixed with potassium cyanide. This mixture was distilled in an iron retort; the oily liquid which came over was heated with caustic potash till free from ammonia. After washing with ether, the potassium salt was acidified and the toluic acid extracted with ether. This was a mixture of paratoluic with either ortho- or metatoluic acid. An easy method of separation was found by treating the calcium salts with alcohol, in which the para salt was not soluble. By this means they obtained, not the meta, but the orthotoluic acid. They further confirmed their work by oxidizing this orthotoluic acid by means of a mixture of potassium bichromate and dilute sulphuric acid, and obtained as a product neither isophthalic nor terephthalic acid, which showed conclusively, that the isomeric acid formed together with paratoluenesulphonic acid when toluene is treated with sulphuric acid, is not the meta, but the para, compound.

The next contribution to our knowledge of the isomeric toluenesulphonic acids, was a consequence of the work of Hübner and Post¹ on bromotoluene and the behavior of its hydrogen atoms.

By the action of sulphuric acid on crystallized bromotoluene, which they showed to be a para compound, two isomeric bromotoluenesulphonic acids were obtained, which they designated as the α - and β -parabromotoluenesulphonic acids. The β -acid was treated with sodium amalgam in order to remove the bromine atom, and the toluenesulphonic acid thus obtained, was fused with potassium hydroxide. Salicylic acid was obtained, which was evidence that the sulphon group was in the position ortho to the methyl group. It was, therefore, by exclusion, concluded that the α -acid must have the sulphon group in the meta position.

F. C. G. Müller² made the barium salt of orthobromotoluene-

¹ Ann. Chem. (Liebig), 169, 47.

² Ibid, 169, 47.

sulphonic acid and treated it, in solution, with sodium amalgam, in order to remove the bromine atom from its molecule. The excess of alkali was neutralized with sulphuric acid, the sodium sulphate removed by evaporation and crystallization, and the residue dried. The dried mass was treated with phosphorus pentachloride, and an oily toluenesulphonchloride was obtained. This was heated with water to 130° , and the resulting acid mixture was freed from hydrochloric acid by evaporation and the passage of a current of air through it. The toluenesulphonic acid was obtained as a syrup, which stiffened to a crystalline condition. Various salts of the acid were made, some of which will be described later on. The amide obtained melted at 90° - 91° . Because this toluenesulphonic acid differed from both the ortho and para acids, Müller considered it to be metatoluenesulphonic acid.

About the same time F. Gerver¹ made orthodiazotoluenesulphonic acid by subjecting orthotoluidinesulphonic acid to the action of nitrous fumes. The diazo compound was decomposed in alcohol under pressure. The sodium salt of the sulphonic acid obtained was made, and gave upon treatment with phosphorus pentachloride, a fluid sulphonchloride, which was converted by the action of ammonia into an amide melting at 148° , and differing in this and other properties, from the ortho and para amides previously known.

In 1874 Pechmann² obtained a quantity of paratoluidine-metasulphonic acid by heating sulphuric acid with paratoluidine, and crystallizing out the paratoluidineorthosulphonic and the disulphonic acids formed, leaving the paratoluidine-metasulphonic acid, on account of its greater solubility, in solution.

From this solution the paratoluidinemetasulphonic acid crystallized out in sulphur-yellow needles which could not be decolorized by repeated boiling with animal charcoal. By precipitation from its salts, however, it was obtained colorless. It was difficultly soluble in cold water, one part of acid requiring ten parts of water for its solution.

The diazo compound was made by suspending the finely divided acid in alcohol, and treating it with nitrous fumes.

¹ Ann. Chem. (Liebig), **169**, 383.

² *Ibid.*, **173**, 195.

This was then decomposed by heating it under pressure with alcohol.

Various salts of the resulting sulphonic acid were made which showed some differences from those of Müller, also an amide which melted somewhat below 100° .

In 1875, Pagel,¹ working on orthotoluidinesulphonic acid, obtained a toluenesulphonic acid which resembled Müller's meta acid.

A mixture of alcohol and sulphuric acid was neutralized with lime, and the resulting calcium ethyl sulphate was decomposed by the addition of a solution of the orthotoluidine salt of oxalic acid. By filtration and crystallization, crystals of orthotoluidine ethyl sulphate were obtained, which were decomposed into alcohol and orthotoluidinesulphonic acid by being heated to 180° – 200° in an air-bath.

The orthotoluidinesulphonic acid was changed into the diazo compound, and this transformed into bromotoluenesulphonic acid.

By proceeding as Müller did, a toluenesulphonic acid was obtained which agreed tolerably well with Müller's metatoluenesulphonic acid, if we except the melting-point of the amide, which Pagel found to be 104° .

In 1877, H. Beckurts,² seeking for a method by which to obtain a good yield of pure orthotoluenesulphonic acid, heated a mixture of ordinary sulphuric acid and toluene and made the potassium salts of the resulting sulphonic acids in the usual manner. By treatment with phosphorus pentachloride a mixture of sulphonchlorides was obtained, from which the paratoluenesulphonchloride crystallized out upon cooling the mixture to 15° below zero.

The remaining liquid sulphonchloride was transformed into the amide compound, which was purified and subjected to fractional crystallization. Two compounds were obtained, one difficultly soluble in alcohol, which melted at 153° – 154° , the other easily soluble in the same medium, and melting at 104° . From this work, Beckurts concluded that the action of sulphuric acid on toluene, resulted in the formation of the three isomeric sulphonic acids. The work was pursued further,

¹ Ann. Chem. (Liebig), 176, 297.

² Ber. d. chem. Ges., 10, 943.

and some of the amide heated with hydrochloric acid in a sealed tube to 150° . The ammonium salt of the acid was thus obtained, and from a portion of this, treated with barium hydroxide, the barium salt. From a comparison of these salts with the ammonium and barium salts obtained by Müller, Beckurts asserts that they were salts of metatoluenesulphonic acid.

Fahlberg,¹ working in this laboratory, doubted the statement that Beckurts had obtained metatoluenesulphonic acid, because, though his product showed differences from the ortho and para compounds, he neglected to prove its constitution by converting it into an oxybenzoic acid. Fahlberg repeated Beckurts' work, with the sole exception that water, and not alcohol, was used as the medium for fractional crystallization.

The liquid sulphonchloride, from which no more solid parasulphonchloride separated out when cooled to 15° below zero, was treated with aqueous ammonia. As products there were obtained α -toluenedisulphonamide, melting at 186° – 187° , and a yellow mixture of amides. This latter he subjected to fractional solution; whereby only a portion dissolved. The undissolved amide melted at 153° – 154° , and gave upon fusing with caustic potash, salicylic acid. Therefore it was orthotoluenesulphonamide. From the soluble portion of the mixture, two compounds were obtained by fractional crystallization. That less soluble, on purification, proved also to be orthotoluenesulphonamide.

From the solution of the more soluble portion an amide crystallized out, which melted at 120° , but repeated purifications from animal charcoal lowered the melting-point to 108° , where it remained constant. A quantity of the amide which melted at 108° was oxidized by means of potassium permanganate, and three products were obtained; parasulphaminebenzoic acid, anhydroorthosulphaminebenzoic acid, and acid potassium orthosulphobenzoate; which were the products one would expect to result from the oxidation of a mixture of para and orthotoluenesulphonamides.

Further evidence that Beckurts' amide, despite the constancy of its melting-point, was a mixture, was given by the follow-

¹ This JOURNAL, I, 179; Ber. d. chem. Ges., 10, 1048.

ing experiment: Equal parts of pure para- and orthotoluene-sulphonamides were dissolved in water and the mixture subjected to recrystallization. Two forms of crystals were obtained: long fine needles which melted constantly at 120° and leaves which fused at 108° . Slight impurities lowered the melting-point to 104° – 105° , as in the case of Beckurt's amide. F. H. S. Müller,¹ in 1879, mentioned the formation of metatoluenesulphonic acid by the action of sulphurous acid on the corresponding diazo compounds; but beyond the melting-points of the amide, anilide and toluidide, gave no details of his work.

Claesson and Wallin,² in 1879, claimed that they had obtained metatoluenesulphonic acid by the action of chlorsulphonic acid on toluene. These investigators worked with large quantities of material, bringing together in small portions at a time, 2800 grams of chlorsulphonic acid and 1119 grams of toluene.

The solid parasulphonchloride was removed by cooling the mixture, and the liquid chlorides converted into the amides. Two amides were separated by fractional crystallization, the ortho compound melting at 153° – 154° , and the other, supposed to be the meta, melting constantly at 107° – 108° . This latter was transformed into the toluenesulphonic acid by being heated with water in a sealed tube to 150° , and various salts were made. These were compared with the salts made by Müller, and also with the analogous salts of the para and ortho acids. From this, despite the fact that they had knowledge of Fahlberg's work, Claesson and Wallin concluded that all three isomeric acids were formed as a result of the action of sulphuric acid on toluene.

The next step in the controversy was taken by R. Otto,³ who, at the request of Beckurts, examined carefully the specimen of so-called metatoluenesulphonamide, which the latter had obtained three years previously, and which was claimed by Fahlberg to be a mixture, and by Claesson and Wallin, to be metatoluenesulphonamide. The substance, weighing about 10 grams, was heated with hydrochloric acid in a sealed tube. The sulphonic acid formed was converted into the potassium

¹ Ber. d. chem. Ges., 12, 1348.

² *Ibid.*, 12, 1848.

³ *Ibid.*, 13, 1292.

salt, and this was treated with phosphorus pentachloride, with the formation of an oil which soon stiffened and the solid portion of which was freed from the fluid by pressure. This latter portion was dissolved in benzene, from which it crystallized out in large scales which had the same melting-point as paratoluenesulphonchloride, and gave a corresponding amide and anilide. This was conclusive evidence that metatoluenesulphonic acid was not obtained by Beckurts.

Neville and Winther,¹ in 1880, investigated the formation of amidosulphonic acids by the action of concentrated sulphuric acid, obtained a toluenesulphonic acid by heating orthodiazotoluenesulphonic acid under pressure with alcohol, and by reducing bromotolueneorthosulphonic acid by means of sodium amalgam. By treating the potassium salt with phosphorus pentachloride they obtained a liquid sulphonchloride which gave, in both cases, an amide melting at $106^{\circ}.5-107^{\circ}.5$, whence they concluded that the acid which they had obtained was metatoluenesulphonic acid.

In 1886, Valin,² convinced by the work of Otto, that Fahlberg's views were correct, and that he and Klason had not obtained metatoluenesulphonic acid, again attacked the problem of obtaining the compound. Pechmann's method was followed; an acid was obtained, and a series of salts made and described.

The work of Metcalf³ furnished evidence that the decomposition of paradiazometatoluenesulphonic acid by boiling with alcohol under pressure, resulted in the formation of parathoxymetatoluenesulphonic acid in far greater proportion than metatoluenesulphonic acid. Consequently, neither by Pechmann nor by Valin had the acid been obtained.

Preparation of Metatoluenesulphonic Acid.

In consideration of all this dissentient testimony in regard to metatoluenesulphonic acid and of the fact that pure metatoluenesulphonamide is now by my researches made available in any desired quantity, it was thought desirable to transform the amide into the acid and study its properties. Sealed tubes containing 25 grams of the pure amide and a quantity of hy-

¹ J. Chem. Soc., 37, 628.

² Ber. d. chem. Ges., 19, 2952.

³ This JOURNAL, 15, 301.

drochloric acid were heated to 140° for six hours. Upon cooling the tubes contained a mass of clear white fern-shaped crystals entirely different in form from the crystals of the amide. These proved to consist entirely of ammonium chloride.

The fluid portion of the contents of the tube was evaporated down on a water-bath, water added and evaporated, and this process repeated until the greater portion of the hydrochloric acid was removed. The solution was then boiled with potassium hydroxide solution until no further evolution of ammonia was evident. The solution, which contained the potassium salt of metatoluenesulphonic acid and some potassium chloride, was then evaporated down until it solidified in a mass of scales. These were powdered and boiled with alcohol of 95 per cent. The greater portion of the salt dissolved, and separated out on cooling, in a mass of minute scales which nearly filled the beaker. From the mother-liquor more of the salt was obtained by evaporation. The undissolved portion was subjected to several more extractions until potassium metatoluenesulphonate no longer crystallized out of the solution. The residue was then examined and found to be potassium chloride. The crystals from the alcoholic solution were collected on a filter and dried. They were then powdered and heated in an air-bath for an hour to 160° . Upon cooling, the substance was rubbed up in a mortar with an equal weight of phosphorus pentachloride. The action was immediate and brisk, and the contents of the mortar became liquid; but the decomposition was not nearly as violent as when the potassium salt obtained from the diazo decomposition was employed. The liquid chloride mixture was poured into water and thoroughly stirred up. A clear, almost colorless oil gathered on the bottom of the vessel. This was washed several times with water, and then placed in a test-tube in a freezing-mixture. It did not solidify. Müller converted the sulphonchloride, which he obtained, into the corresponding acid by heating it with water in a sealed tube. He stated that it did not decompose with water until it was heated to 130° .

About 5 cc. of the sulphonchloride and 100 cc. of water

were placed in a flask connected with an inverted condenser and boiled. Considerable bumping occurred, a small portion of the contents of the flask at times fuming out through the top of the condenser. In about an hour and a half the oily liquid had entirely disappeared. The solution was then poured into an evaporating dish and boiled until it attained a syrupy consistency. More water was added and it was again evaporated down. This process was repeated until the solution gave no indication of the presence of hydrochloric acid when tested with silver nitrate. An effort to obtain the metatoluenesulphonic acid in crystalline condition was unsuccessful. After it had become viscous, further heating on a water-bath resulted in giving it a dark, almost black, color. Made clear by boiling with animal charcoal and filtering, it darkened again when kept on the water-bath.

Efforts were then made to crystallize it by evaporation under diminished pressure. About 15 cc. of the syrupy liquid was placed in a round-bottomed flask, which was connected to a filter-pump and kept in boiling water for over an hour. On cooling the contents of the flask remained fluid. The viscous liquid was then placed in a test-tube, and kept in a freezing-mixture for half an hour, and though its temperature was lowered to 18° below zero, its condition did not change.

Müller, Von Pechmann, Pagel, and Klason, all obtained, by evaporating down their acid solutions, a syrup which stiffened to a mass of deliquescent crystals.

Barium Salt of Metatoluenesulphonic Acid.—A solution of the acid was heated to boiling, and neutralized with barium carbonate. The solution was then filtered and evaporated down to a small bulk. On cooling, the barium salt crystallized out in minute crystals. With favorable conditions, bunches of apparently rectangular plates about $\frac{1}{8}$ of an inch long, were obtained. It is very soluble in water, insoluble in absolute alcohol and ether; soluble in dilute alcohol, and precipitated from its solution in the latter by the addition of a large quantity of ether.

It contained one molecule of water of crystallization.

The salt was analyzed with the following results:

I. 0.2702 gram of the salt gave off, at 180°, 0.0101 gram of water.

II. 0.2208 gram of the salt gave off, at 180°, 0.0080 gram of water.

III. 0.2702 gram of the salt gave 0.1260 gram of barium sulphate.

IV. 0.2208 gram of the salt gave 0.1030 gram of barium sulphate.

	Calculated for (C ₈ H ₄ <CH ₃) ₄ Ba+H ₂ O.	I.	Found. II.
H ₂ O	3.62	3.73	3.62
Ba	27.56	27.42	27.42

The barium salt, made by Müller by boiling the free acid with pure barium carbonate, gave off two molecules of water of crystallization. Neither from water nor from alcohol could he obtain it in a distinctly crystalline condition.

Lead Salt.—This salt, which was very soluble in water, and slightly soluble in strong alcohol, was obtained in the form of a mass of crystals consisting of small scales. The addition of a large quantity of ether to its dilute alcoholic solution precipitated it in scales. The analysis of the salt was made with the following results:

For water of crystallization:

I. 0.2480 gram of salt, heated to 160°, gave off 0.0078 gram of water.

II. 0.2394 gram of salt gave off 0.078 gram of water.

III. 0.2212 gram of salt gave off 0.0070 gram of water.

IV. 0.2480 gram of the anhydrous salt gave 0.1278 gram of lead sulphate.

V. 0.3538 gram of the salt gave 0.1813 gram of lead sulphate.

VI. 0.3781 gram of the salt gave 0.1923 gram of lead sulphate.

	Calculated for (C ₈ H ₄ <CH ₃) ₄ Pb+H ₂ O.	I.	Found. II.	III.
H ₂ O	3.17	3.14	3.17	3.16
Pb	36.33	35.21	35.57	34.74

In describing his lead salt, Müller calls attention to the fact that the anhydrous salt absorbed moisture very rapidly, which

made it difficult to get good results for the water of crystallization. No such behavior was noticed in the case of the lead salt here described. The results in water of crystallization agreed as closely as possible with the theoretical, and no difficulty in weighing was experienced. On the other hand, it was found impossible to get good results in the determination of lead. Many analyses were made, the three given above being the best results obtained. Ignition of the salt, alone, or when moistened with sulphuric or nitric acid, invariably caused some reduction. Precipitation in alcoholic solution, as lead sulphate, and filtration through a Gooch crucible, gave no better results.

Calcium Salt.—The calcium salt was made by decomposing finely powdered calcite by means of the free acid. It was extremely soluble in water, and could be obtained in crystalline condition only by evaporating the solution almost to dryness, when, upon cooling, it solidified in a mass of scales, which were so matted together that they could not be obtained in dry condition, by long standing in the air. Upon heating a saturated solution of the calcium salt, a slight milky precipitation occurred, which disappeared on standing, indicating its greater solubility in cold than in hot water. Analyses were made of a specimen which had been dried by standing over sulphuric acid.

I. 0.3989 gram of the calcium salt, heated to 200°, lost 0.0343 gram of water.

II. 0.3196 gram of the calcium salt, heated to 200°, lost 0.0270 gram of water.

III. 0.3989 gram of the salt gave 0.1210 gram of calcium sulphate.

IV. 0.3196 gram of the salt gave 0.1051 gram of calcium sulphate.

	Calculated for ($C_6H_4<\begin{smallmatrix} CH_3 \\ SO_3 \end{smallmatrix}$)Ca+2H ₂ O.	Found.	
		I.	II.
H ₂ O	8.61	8.59	8.44
Ca	9.57	9.66	9.67

Müller did not succeed in obtaining the calcium salt of its toluenesulphonic acid in crystalline condition from its solution in water, and his salts, whether obtained by evaporating

the water solution to dryness or by filtering the boiling alcoholic solution through a warmed filter, continued to give off water when heated to 200°.

The salt, the analysis of which is given above, was easily obtained in crystalline condition, and gave off all its water of crystallization at 180–190°; and heated to 200°, it began to darken in color. It was evidently a different compound from that of Müller.

Sodium Salt.—The sodium salt was made by exactly precipitating the barium by means of sodium sulphate from a solution of the barium salt. It is very soluble in water, from which it crystallizes out in large scales when the solution is evaporated down.

Its analysis resulted as follows:

I. 0.1641 gram of salt lost, upon heating to 150°, 0.0139 gram of water.

II. 0.2060 gram of salt gave off 0.0175 gram of water.

III. 0.1502 gram of the salt gave 0.0549 gram of sodium sulphate.

IV. 0.1885 gram of the salt gave 0.0683 gram of sodium sulphate.

	Calculated for ($C_8H_4<CH_3$) SO_3)Na+H ₂ O.	I.	Found. II.
H ₂ O	8.49	8.47	8.49
Na	10.85	10.91	10.73

The sodium salt obtained by Müller did not crystallize well from water, and contained but one-half a molecule of water of crystallization.

Potassium Salt.—The potassium salt was made, as was the sodium, by the exact precipitation of a solution of the barium salt. This salt crystallized in thin scales and was easily soluble in water, sparingly so in strong alcohol. It dissolved to a great extent in hot, ordinary alcohol, from which it separated out in small scales. Addition of ether to the alcoholic mother-liquor caused a copious precipitation.

The following are the results of its analysis:

I. 0.2146 gram of the salt, heated to 180°, gave off 0.0096 gram of water.

II. 0.1980 gram of the salt gave off 0.0089 gram of water.

III. 0.2146 gram of the salt gave 0.0844 gram of potassium sulphate.

IV. 0.1980 gram of the salt gave 0.0773 gram of potassium sulphate.

	Calculated for $C_6H_4<\overset{CH_3}{SO_3}K + \frac{1}{2}H_2O$.	Found.	
		I.	II.
H ₂ O	4.11	4.47	4.49
K	17.75	17.63	17.50

This potassium salt agrees with that of Müller in solubility and water of crystallization.

Silver Salt.—Pure silver carbonate, obtained by precipitating a solution of silver nitrate by means of sodium carbonate, was decomposed in a boiling solution of the acid. Upon filtering and evaporating down to a small volume, bunches of rectangular plates were obtained, which showed a micaceous cleavage. These were easily soluble in water, and to a much less extent in alcohol. From their solution in the latter they were precipitated by the addition of ether. They contained no water of crystallization, and blackened on exposure to the light.

I. 0.2061 gram of the salt gave 0.0080 gram of silver.

II. 0.2640 gram of the salt gave 0.1023 gram of silver.

	Calculated for $C_6H_4<\overset{CH_3}{SO_3}Ag$.	Found.	
		I.	II.
Ag	38.71	38.81	38.75

Magnesium Salt.—The magnesium salt was made by boiling pure magnesium carbonate in a solution of the acid. After neutralizing the acid the solution was filtered, and reduced in volume by evaporation. On standing, the salt crystallized out in beautiful, long, transparent, thick prisms, which lost water rapidly in the air. Their crystalline structure appeared to be orthorhombic and hemihedral. The magnesium salt is slightly soluble in alcohol, from which it is precipitated by ether in minute plates. The property of rapidly losing water of crystallization, when exposed to the air, was not noticed in any of the other salts of metatoluenesulphonic acid. But the magnesium salt, which consisted of beautiful, large, transparent crystals, some of them an inch and over in length when first removed from the mother-liquor, became opaque

after brief exposure to the air, and disintegrated upon long standing.

Subjected to analysis it yielded the following results:

I. 0.2050 gram of the salt lost, when heated to 150° , 0.0644 gram of water.

II. 0.2166 gram of the salt gave off, at the same temperature, 0.0691 gram of water.

III. 0.2636 gram of the anhydrous salt gave 0.0865 gram of magnesium sulphate.

IV. 0.2797 gram of the anhydrous salt gave 0.0896 gram of magnesium sulphate.

	Calculated for $(C_6H_4<\overset{CH_3}{SO_2})_2Mg+10H_2O$.	I.	Found. II.
H ₂ O	32.05	31.45	31.90
Mg	6.56	6.55	6.40

Manganese Salt.—A solution of the barium salt was treated to exact precipitation with manganous sulphate. On reducing the solution to a small bulk and cooling, the manganese salt crystallized out in long prisms, which were easily soluble in water, and to a slight extent in alcohol. From the alcoholic solution they were precipitated in the form of bunches of small needles.

The following are the results of the analyses:

I. 0.2150 gram of the salt gave off, when heated to 200° , 0.0461 gram of water.

II. 0.2708 gram of the salt gave off 0.0588 gram of water.

III. 0.2150 gram of the anhydrous salt gave 0.0326 gram of manganous manganic oxide.

IV. 0.1689 gram of the salt gave 0.0326 gram of manganous manganic oxide.

	Calculated for $(C_6H_4<\overset{CH_3}{SO_2})_2Mn+6H_2O$.	I.	Found. II.
H ₂ O	21.44	21.44	21.67
Mn	10.89	10.92	10.93

Zinc Salt.—The zinc salt was made by treating a boiling solution of the acid with pure zinc carbonate. After filtering and evaporating down the solution, long, slender prisms were deposited. They were soluble in water and alcohol, and were precipitated from the alcoholic solution in minute scales on

the addition of ether. The salt was very stable, and the crystals retained their lustre after long exposure to the air. It was analyzed for zinc, by precipitating as carbonate and igniting.

I. 0.3377 gram of the salt lost, upon being heated to 180° , 0.0695 gram of water.

II. 0.3106 gram of the salt lost, upon being heated to 180° , 0.0638 gram of water.

III. 0.3377 gram of the salt gave 0.0527 gram of zinc oxide.

IV. 0.3106 gram of the salt gave 0.0482 gram of zinc oxide.

	Calculated for ($C_6H_4<\begin{smallmatrix} CH_3 \\ SO_3 \end{smallmatrix}$) ₂ Zn+6H ₂ O.	Found.	
		I.	II.
H ₂ O	20.97	20.58	20.54
Zn	12.62	12.51	12.52

Copper Salt.—On evaporating a solution of this salt nearly to dryness and cooling, a mass of light blue scales was obtained. The copper salt was very soluble in water and ordinary alcohol, very slightly soluble in absolute alcohol, and insoluble in ether. The addition of ether to an alcoholic solution of the salt caused its precipitation in minute, almost white, scales. No very satisfactory determination of water of crystallization of the copper salt could be obtained.

On heating 0.2995 gram of the salt to constant weight in an air-bath at 170° , it was found to have lost 0.0450 gram of water, or 15.02 per cent. The theoretical percentage of water, assuming the salt to contain four molecules of water of crystallization is 15.03. The determination of the water of crystallization of different specimens obtained by precipitating the salt from its alcoholic solution by means of ether, gave no concordant results.

The copper was determined in the anhydrous salt by electrolysis.

I. 0.2545 gram of the anhydrous salt gave 0.0401 gram of copper.

II. 0.3725 gram of the salt gave 0.0585 gram of copper.

	Calculated for ($C_6H_4<\begin{smallmatrix} CH_3 \\ SO_3 \end{smallmatrix}$) ₂ Cu.	Found.	
		I.	II.
	15.55	15.70	15.70

Metatoluenesulphonanilide.—This substance was made by

bringing together some metatoluenesulphonchloride and a slight excess of aniline. The action was extremely rapid. The flask became very hot and its contents solidified to a crystalline mass. The contents of the flask were then boiled with dilute hydrochloric acid, in order to remove any unacted upon aniline, and the anilide was then crystallized from ether, in which it was very soluble. A yield of small prismatic crystals was obtained. The anilide was insoluble in cold water, and dissolved only to a very slight extent in boiling water. It was extremely soluble in alcohol, from which it crystallized out in large monoclinic prisms. It melted sharply at 96° .

Müller and Wiesinger¹ mention a metatoluenesulphonanilide, which melted at 72° . They obtained their meta acid by treating their diazo compound with sulphurous acid.

Metatoluenesulphontoluide.—The ortho- and paratoluides of metatoluenesulphonic acid were made by bringing together metatoluenesulphonchloride and the proper toluidine, the latter in slight excess. The reaction was very rapid and violent, part of the contents of the flask volatilizing. The excess of toluidine was removed by warming the mixture with dilute hydrochloric acid, and washing several times with water. Both toluides are well crystallized compounds, insoluble in water, but very soluble in ether, alcohol, and benzene.

The metatoluenesulphonorthotoluide crystallizes in prisms and thick plates, and melts at 108° .

The metatoluenesulphonparatoluide crystallizes in small prisms and melts at 106° . The toluidine mentioned by Müller and Wiesinger² melted at 103° .

Conclusion.

From the study of metatoluenesulphonic acid and its salts, we may conclude that the compounds obtained by Müller and others who employed analogous methods for obtaining them, were impure products.

This follows especially from a comparison of the properties of the amide, and from the fact that the sulphonchloride suffers decomposition into the acid when boiled with water in an open vessel, while the sulphonchloride of Müller did not decompose until heated to 130° in a sealed tube.

¹ Ber. d. chem. Ges., 12, 1348.

² Loc. cit.

No detailed comparison of the salts of the metatoluenesulphonic acid herein described, with those made by other methods than those of Müller was made, for previous work in this laboratory, by Fahlberg and Metcalf showed conclusively that they were not true meta compounds.

JOHNS HOPKINS UNIVERSITY,
JUNE, 1895.

Contributions from the Chemical Laboratory of Harvard College.

XCVII.--ON THE COLORED COMPOUNDS OBTAINED
FROM SODIC ETHYLATE AND CERTAIN
AROMATIC NITRO COMPOUNDS.¹

BY C. LORING JACKSON AND MARTIN H. ITTNER.

The formation of strikingly colored substances by the action of alkaline solutions on certain aromatic nitro compounds was first mentioned, so far as we can find, by H. Salkowski² in his paper on "Chrysanisic Acid," where he described the nearly black compound formed from chrysanisic acid, the reddish purple one from dinitranisic acid and the rose-colored derivative of ethoxydinitrobenzoic ethylester. Hepp³ also observed the appearance of a blood-red color when symmetrical trinitrobenzol was treated with potassic or ammoniac hydrate.

Much more recently, Victor Meyer⁴ called attention to the curious phenomena attending the action of sodic hydrate on symmetrical dinitrobenzoic acid, which with one equivalent or less of alkali gave a colorless solution, with more dilute alkali a yellowish-red color, and with an excess of strong alkali a dark violet solution, but this latter color faded in a short time, and the solution became colorless again. After longer standing of the same solution it took on a permanent fuchsine-red color. He connected these phenomena with the colors obtained from symmetrical trinitrobenzol with alkalis, and suggested that the fugitive color might be due to a salt formed through the replacement by sodium of the hydrogen standing upon the benzol ring between the two nitro groups. In continuation of this work Shukoff⁵ has studied under Vic-

¹ Part of the work described in this paper was included in a thesis presented to the Faculty of Arts and Sciences of Harvard University for the degree of Doctor of Philosophy, by Martin H. Ittner.

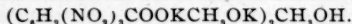
² Ann. Chem. (Liebig), **163**, 49, 52, 56.

⁴ Ber. d. chem. Ges., **27**, 3153.

³ Ibid. **215**, 359.

⁵ Ibid. **28**, 1800.

tor Meyer's direction the fuchsine-red solution, and has found that it contains the two new acids, dinitroazoxybenzoic acid and azoxytrihydroxybenzoic acid. Shortly after the appearance of the paper by Victor Meyer, C. A. Lobry de Bruyn¹ published a paper in which he described a series of experiments on these substances begun six years before. These included the observation that nitro compounds, which give the red color with alkalies, are not acted on by metallic sodium, even when the solution in xylol is boiled with it; and that potassic hydrate formed red crystals with a solution of symmetrical trinitrobenzol in methyl alcohol, whereas no such compound was formed with sodic hydrate. He also observed that the formation of the red compound was accompanied or rather followed by that of potassic nitrite. In a later paper Lobry de Bruyn and Van Leent² succeed in analyzing these red crystals, which have the formula $C_6H_3(NO_2)_3K(OH, \frac{1}{2}H_2O)$. In a subsequent paper³ Victor Meyer points out that this compound can also be considered $C_6H_3K(NO_2)_3CH_2OH \frac{1}{2}H_2O$; and shows that sodic nitrite is not eliminated by the action of sodic hydrate in aqueous solution on symmetrical trinitrobenzol, if the test is made at once, and the alkali is not too strong, thus confirming the observation of Lobry de Bruyn, which is described in the paper⁴ just cited. F. H. van Leent⁵ has recently analyzed another of these compounds obtained by the action of potassic hydrate in methyl alcohol solution on trinitrobenzoic acid, $(CO_2H, (NO_2)_3, 1, 2, 4, 6)$, and found that its formula is



We should perhaps add to the list of these bodies the dark-green compound formed by the action of sodic or ammoniac hydrate on bromdinitrophenylacetic acid, discovered by W. S. Robinson and one of us,⁶ since there was some evidence that the normal salt of this substance might be colorless, and also the unstable red substance formed by an excess of alkali and dichlorodinitrophenylacetic acid observed by W. R. Lamar

¹ Rec. Trav. Chim. Pays. Bas., 14, 89.

² *Ibid.*, 14, 150; Ber. d. chem. Ges., '96, R. 40.

³ Ber. d. chem. Ges., 29, 848.

⁴ *Ibid.*, 15, 89.

⁵ Rec. Trav. chim. Pays Bas., 14, 91.

⁶ This JOURNAL, 11, 553.

and one of us.¹ In this latter case a colorless salt was formed when the alkali was not added in excess.

Our attention was called to this subject by the discovery of a number of brilliantly colored derivatives from parabromdimetanitrotoluol and related substances. After we had made some progress in the study of these compounds, our work was brought to an end by the paper of Victor Meyer, already mentioned. We accordingly, after some delay, published a notice² of what we had done, with the statement that we withdrew in order not to interfere with the chemists, who had already occupied this field. This notice brought us at once a letter from Lobry de Bruyn, in which he told us that Victor Meyer had left to him the study of the colors formed with sodic alcoholates, and in the most generous way asked us to continue our research. We are glad to have this opportunity of expressing our warmest thanks to him for his great courtesy and liberality. Unfortunately, our time was so occupied after we received permission to continue the work, that we could devote only a month to it, but in that time we have collected enough facts to make it worth while to publish this paper, especially as we shall be unable to continue the work together.

The colors discovered by us are collected in the following table, in which the first column gives the formula of the substance, which was converted into the colored compound by the action of a strong alcoholic solution of sodic ethylate, the second the color obtained, and the third the stability, which we have expressed roughly by stating whether the color lasted for several seconds, for several minutes, or under favorable conditions for several hours. The precautions necessary in order to obtain some of these substances will be found in the experimental part of this paper. All these substances have the constitution CH_3 (or COOH) $\cdot$ NO_2 $\cdot$ X $\cdot$ NO_2 .

Substance.	Color.	Stability.
$\text{BrC}_6\text{H}_4(\text{NO}_2)_2\text{CH}_3$	Blue	Seconds
$\text{C}_6\text{H}_4\text{NHC}_6\text{H}_4(\text{NO}_2)_2\text{CH}_3$	Green	Seconds
$\text{NH}_2\text{C}_6\text{H}_4\text{NHC}_6\text{H}_4(\text{NO}_2)_2\text{CH}_3$	Green	Seconds
$\text{C}_6\text{H}_4\text{Br}_2\text{NHC}_6\text{H}_4(\text{NO}_2)_2\text{CH}_3$	Purple	Minutes

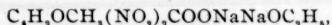
¹ This JOURNAL, 18, 681.

² Ber. d. chem. Ges., 28, 3063.

Substance.	Color.	Stability.
$\text{NH}_2\text{C}_6\text{H}_4\text{Br}, \text{NHC}_6\text{H}_4(\text{NO}_2), \text{CH}_3$	Bluish purple	Minutes
$\text{BrC}_6\text{H}_4(\text{NO}_2), \text{COOH}$	Reddish purple	Hours
$\text{BrC}_6\text{H}_4(\text{NO}_2), \text{COOC}_2\text{H}_5$	Rose	Hours
$\text{C}_6\text{H}_5\text{NHC}_6\text{H}_4(\text{NO}_2), \text{COOH}$	Pansy purple	Hours
$\text{C}_6\text{H}_5\text{NHC}_6\text{H}_4(\text{NO}_2), \text{COOC}_2\text{H}_5$	Cherry red	Hours
$\text{CH}_3\text{OC}_6\text{H}_4(\text{NO}_2), \text{COOH}$	Reddish purple	Hours
$\text{C}_6\text{H}_5\text{OC}_6\text{H}_4(\text{NO}_2), \text{COOH}$	Reddish purple	Hours
$\text{C}_6\text{H}_5\text{OC}_6\text{H}_4(\text{NO}_2), \text{COOC}_2\text{H}_5$	Rose	Hours
$\text{NH}_2\text{C}_6\text{H}_4(\text{NO}_2), \text{COOH}$	Black	
$\text{NH}_2\text{C}_6\text{H}_4(\text{NO}_2), \text{COOC}_2\text{H}_5$	Red	

These substances fall into three groups, so far as stability goes. The substituted toluols gave very unstable compounds, which faded usually in about ten seconds, unless one of the substituting radicals was a tribromanilido group, in which case somewhat more stable compounds were formed; but these were far inferior in stability to the derivatives of the substituted benzoic acids, which kept, even when moist, for half an hour or more, and, when purified and dried, lasted often for several days. All of these substances, however, decomposed spontaneously in time, and were almost instantaneously decomposed by water or acids, giving the original substance, unless this had been affected by a secondary reaction.

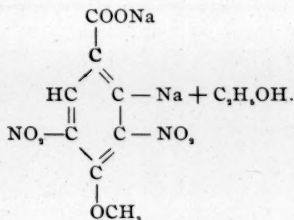
We succeeded in preparing the colored compound from dinitranisic acid in a state fit for analysis by precipitating the alcoholic solution of it with ligroin. The analyses of the substance dried *in vacuo* led to the formula



in the form of which we do not intend to commit ourselves to any theory of the constitution of the substance, but merely to indicate that it amounts to the sodic dinitranisate with the addition of the elements of one molecule of sodic ethylate. If heated to 110° it lost a weight nearly corresponding to one molecule of alcohol, and the residue contained an amount of sodium corresponding to the formula $\text{C}_6\text{H}_5\text{OCH}_2(\text{NO}_2)_2\text{COONa}$. This substance, however, did not dissolve in alcohol with the purple color of the original body, but had a brown color, which indicated decomposition. In one case we thought we

detected an odor of formaldehyde, while heating the compound to 110° , but we have never observed it again. In a later determination we collected the substance volatilized, and tested it with ammoniac hydrate for formaldehyde. The result showed, that if there was any present, it could not amount to more than one per cent. The principal part of the substance given off was alcohol, to judge from its very evident odor and the iodoform test.

The only theory to account for these products, which has been published in any detail, is that advanced by Victor Meyer, who looked upon them as salts formed by the replacement of an atom of hydrogen on the benzol ring by an atom of sodium or potassium. As stated by him, this hypothesis is not applicable to the substances described in this paper, since he considered that the hydrogen replaced was that standing between the two nitro groups in dinitrobenzoic acid or trinitrobenzol, and none of our compounds contain such an atom of hydrogen, the position between the two nitro groups being occupied by some other radical (Br , $\text{C}_6\text{H}_5\text{NH}$, CH_3O , or some others), which is not replaced by sodium, as the original substance can be regenerated from the colored compounds without difficulty. A slight modification of this hypothesis, however, renders it applicable to our compounds. This consists in supposing that the hydrogen between a nitro group and the methyl or carboxyl radical is the one replaced by the metal. If this view is adopted, the formula of the compound from dinitranisic acid would become



This hypothesis has much to recommend it, as it would lead us to expect a strongly colored compound, from which

water or acid would easily regenerate the mother substance, and that the compounds containing the negative carboxyl would be more stable than those containing methyl. Further the fact observed by us that alcohol is given off on heating this substance seems to indicate that it contains alcohol of crystallization. On the other hand there are observations which tell against this hypothesis; thus according to it we must assume one molecule of alcohol of crystallization in each of the substances analyzed, a similarity of composition, which is certainly improbable in compounds derived from such different bodies; while in regard to the substance analyzed by Lobry de Bruyn and Van Leent, the still more improbable assumption must be made that it contains at the same time alcohol and water of crystallization. A much stronger objection than these, however, exists in the fact observed by Lobry de Bruyn that sodium does not act on trinitrobenzol even at the boiling-point of xylol. In fact this seems almost conclusive against the hypothesis that these bodies are formed by the replacement of hydrogen by sodium.

We have also studied the spontaneous decomposition of the reddish-purple compound derived from bromdinitrobenzoic acid and sodic ethylate. This, when in contact with sodic ethylate, gradually changes without alteration of its color into a mixture of sodic bromide, and the colored compound from ethoxydinitrobenzoic acid. Acidification then gives the parethoxydimetanitrobenzoic acid, which melts at 192° , and had not been made previously, so far as we can find. If the mixture is allowed to stand for a longer time, it is converted into paroxydimetanitrobenzoic acid and sodic bromide. This change is indicated by the dark brown color which the mass assumes.

In the hope of finding an easy method of preparing parethoxydimetanitrobenzoic ethylester, we studied the action of hydrochloric acid and alcohol at 100° on chrysanisic ester, and found that in this way a little of the ethoxy ester and ammoniac chloride was formed, but the yield is so small that the process is of no practical value.

EXPERIMENTAL PART.

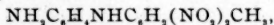
Description of the Colored Compounds.

From Parabromdimetanitrotoluol, $C_6H_4Br(NO_2)_2CH_3$.—If an excess of a concentrated alcoholic solution of freshly prepared sodic ethylate was poured over a little dry bromdinitrotoluol, at first no marked effect was noticed, but if, after the mixture had stood about two minutes, two or three times as much absolute alcohol was added, and the whole well shaken, the liquid took on such an intense dark blue color as to be nearly opaque. The color thus produced was as vivid as that of the more lively aniline blues. This marked color lasted for about ten seconds, at the end of which time it had entirely vanished, leaving a colorless liquid mixed with unaltered bromdinitrotoluol, which is not easily soluble in alcohol. Further addition of sodic ethylate, alcohol, or bromdinitrotoluol failed to produce a reappearance of the color. We cannot state whether the whole of the bromdinitrotoluol was recovered unchanged; certainly most of it was left in the original condition, but a small part may have undergone some permanent change. This, however, if it took place, did not consist in the removal of the bromine or nitro groups from the molecule, as we could get no test for a bromide or nitrite in the aqueous washings of the residue, if the reaction had been stopped as soon as the color vanished. If, on the other hand, the solution of sodic ethylate was allowed to stand for some time with the bromdinitrotoluol, another reaction set in, as was shown by the formation of an abundance of sodic bromide. The organic products of this second reaction have not yet been analyzed. They are not dinitrocresol (or ethoxydinitrotoluol), as far as we could judge from some preliminary work upon them.

The blue compound described above did not appear unless the conditions given were observed with a great deal of care. Dilution, or the addition of an acid, decolorized it instantly. Sodic methylate gave a similar blue compound, and so did sodic amylate, but this latter was more stable than that derived from the ethylate.

From Anilidodinitrotoluol, $C_6H_5NHC_6H_4(NO_2)_2CH_3$. *Melting-point* 169°.—When an excess of a sodic alcoholate was

poured on dry anilidodinitrotoluol the orange crystals became coated with a dark green substance, some of which also dissolved in the alcohol. The color vanished in a very short time, instantly on dilution with a large quantity of absolute alcohol, although the addition of a small quantity intensified the color. *Amidophenyleneimidodinitrotoluol*,



melting-point 185° , gave under the same conditions an exactly similarly-colored compound.

Tribromanilidodinitrotoluol, $\text{C}_6\text{H}_3\text{Br}_3\text{NHC}_6\text{H}_4(\text{NO}_2)_2\text{CH}_3$, melting-point 238° , and *tribromamidophenyleneimidodinitrotoluol*, $\text{NH}_2\text{C}_6\text{H}_3\text{Br}_3\text{NHC}_6\text{H}_4(\text{NO}_2)_2\text{CH}_3$, melting at 222° , gave with an alcoholic solution of sodic ethylate, the first, a purple color, the second, a bluish-purple color. Both these colors were more stable than those described previously, they lasted longer, and no careful observance of conditions was necessary in preparing them; in fact colors were obtained with alcoholic potassic hydrate, but not with sodic hydrate. Also the residue left after the alcohol had evaporated gave the color again upon addition of more of the solution of sodic ethylate. The absolute stability of the colors, however, was slight, as they were decomposed on spontaneous evaporation of the solution, and instantaneously by the addition of water or an acid.

From Parabromdimetanitrobenzoic Acid, $\text{C}_6\text{H}_3\text{Br}(\text{NO}_2)_2\text{COOH}$.—When a strong alcoholic solution of sodic ethylate was added to dry bromdinitrobenzoic acid or one of its salts, an intense reddish-purple color was developed throughout the solution. The color was like that of monomethylrosaniline. This color was formed easily, no precautions being necessary to obtain it, and, as it was very intense, we have used it to advantage as a delicate test for the presence of bromdinitrobenzoic acid. The colored body, like the acid from which it was formed, was easily soluble in alcohol, but could be obtained as a purple crystalline mass by cooling very concentrated alcoholic solutions. It was decomposed instantly by the addition of water, a colorless solution of sodic bromdinitrobenzoate being formed. Acids also decolorized it at once, converting it into bromdinitrobenzoic acid. These observations show plainly

that this colored compound was a derivative of bromdinitrobenzoic acid, and this view was confirmed by the fact that no test for sodic bromide could be obtained from the water, which had been used to decompose the color, if it had been applied immediately after its formation. If, on the other hand, the colored compound was allowed to stand for ten minutes, a distinct test for sodic bromide was obtained from the water used to decompose it; and the amount of this bromine increased with the length of time that the color stood before it was decomposed. As this formation of sodic bromide was accompanied by no perceptible change of color, we are inclined to think that the purple derivative of bromdinitrobenzoic acid decomposed forming sodic bromide and the derivative of ethoxydinitrobenzoic, which has the same color as the original colored substance. The substance retained its reddish purple color for more than half an hour under ordinary conditions. If allowed to stand moist with alcohol for a longer time, a marked change from reddish purple to reddish brown was observed, which was rendered complete by allowing the liquid to evaporate to dryness in the air, or to stand in a corked flask for twenty-four hours. We have succeeded in detecting in this decomposed product, ethoxydinitrobenzoic acid, oxydinitrobenzoic acid, and sodic bromide. The identification of these substances will be discussed in a later paragraph. No test was obtained for sodic nitrite, or for oxalic acid, which would probably have been one of the products, if an azoxy compound had been formed. Sodic methylete behaved like sodic ethylete.

The bromdinitrobenzoic ester, $C_6H_3Br(NO_2)_2COOC_2H_5$, melting at 105° , gave with sodic ethylete in alcoholic solution a beautiful pink color like that of eosine. On standing, this pink color gradually passed into the reddish purple of the derivative from the free acid showing that the ester had been saponified.

Anilidodinitrobenzoic acid, $C_6H_4C_6H_4NH(NO_2)_2COOH$, melting-point 239° , gave with a strong solution of sodic ethylete a bluish purple colored compound, which resembled the the color of a pansy. This substance, which was fairly stable retaining its color for more than half an hour, was very

slightly soluble in alcohol, in this respect resembling the acid from which it was obtained. We could not, therefore, prepare it pure, as orange streaks of the sodium salt of the acid were visible even in our most carefully prepared specimens. We tried dissolving the anilidodinitrobenzoic acid in benzol or acetone before adding the sodic ethylate, in the hope of getting a complete reaction, but under these conditions, although the colored substance was formed, it vanished in less than two minutes. That the substance formed from the anilido acid is more stable even than that from the brom acid was shown by the fact that a bluish purple coloration was obtained with aqueous sodic hydrate. The anilidodinitrobenzoic ester, $C_6H_5NHC_6H_4(NO_2)_2COOC_2H_5$, melting at 154° , gave a cherry-red compound with sodic ethylate, which was as slightly soluble in alcohol as the product from the corresponding acid.

Dinitranisic acid $C_6H_5OCH_3(NO_2)_2COOH$, and *ethoxydinitrobenzoic acid*, $C_6H_5OC_2H_5(NO_2)_2COOH$, melting at 192° , gave with an alcoholic solution of sodic ethylate reddish purple compounds similar to that from bromdinitrobenzoic acid; in fact it is probable that the colored product obtained from this latter body is, after the very first, a mixture of the color from the ethoxy acid and sodic bromide. When the colored compound from dinitranisic acid is treated with hydrochloric acid, the dinitranisic acid is regenerated. Both these colors are comparatively stable, keeping in alcohol for over half an hour, and when carefully purified and dried, even for several days. Similar colored compounds were obtained with sodic methylate or alcoholic potash, as was found previously in the case of the dinitranisic acid by Salkowski,¹ who also observed that the ethoxydinitrobenzoic ethylester, $C_6H_5OC_2H_5(NO_2)_2COOC_2H_5$, gave with sodic ethylate a bright red-rose color.² This color was so similar to that given by the bromdinitrobenzoic ester, that they could not be distinguished by the eye alone.

Salkowski³ also stated that chrysanisic acid, $C_6H_5NH_2(NO_2)_2COOH$, was colored almost black by potassic hydrate in aqueous or alcoholic solution. We repeated this work in

¹ Ann. Chem. (Liebig), 163, 57.

² Ibid, 49.

³ Ibid, 52.

order to see whether this substance would be adapted for analysis, and to confirm his observations. The yellow crystals of chrysanisic acid, when dropped into an alcoholic solution of sodic ethylate, turned black, and the liquid close to the crystals was seen by the microscope to be dark blue-violet. This color, however, did not spread through the solution, either because the substance was very slightly soluble, or because it was decomposed by the liquid. The chrysanisic ethylester, $C_6H_5NH_2(NO_2)_2COOC_2H_5$, melting at 114° , gave a red color with the alcoholic solution of sodic ethylate similar to that obtained from the anilido ester. Oxydinitrobenzoic acid, melting at 245° – 246° , gave no colored compound of this class with sodic ethylate, that we could find, the only product being the brown salt. From mononitranisic acid and nitrosanilidodinitrotoluol also we could not obtain any colored compounds.

Composition of the Colored Compound Made from Dinitranisic Acid and Sodic Ethylate.

After a careful consideration of the colored compounds just described, and a series of experiments, which served to show that many of them were not fitted for analysis, we decided that the one which could be most easily prepared for analysis was that derived from dinitranisic acid.

Preparation of Dinitranisic Acid.—This substance was made according to Salkowski,¹ as follows: Oil of anise was heated with nitric acid of specific gravity 1.4 in a flask, and the product, chiefly mononitranisic acid, after drying, was allowed to stand in the cold for 48 hours with a mixture of nitric acid of specific gravity 1.5, and sulphuric acid. There was a rapid evolution of carbonic dioxide when the substances were mixed, and this could not be prevented by adding the solid in small quantities and careful cooling. The organic product of this reaction was precipitated by pouring the acid liquid into a large amount of cold water, and the precipitate treated with a cold dilute solution of sodic carbonate, which dissolved the dinitranisic acid, but left behind the dinitro and trinitranisol also formed in the process. The dinitranisic acid, precipi-

¹ Ann. Chem. (Liebig), 163, 7.

tated with hydrochloric acid, was purified by recrystallization from dilute alcohol until it melted constant at 179° . The yield obtained by this process is poor, but it is much better than that obtained by acting on bromdinitrobenzoic acid with sodic methylate, as in that case most of the dinitranisic acid was saponified to oxydinitrobenzoic acid during the operation.

Preparation of the Colored Compound.—Six grams of the dinitranisic acid were put into a glass-stoppered bottle of 250 cc. capacity, and dissolved in about 20 cc. of absolute alcohol. The sodic ethylate, prepared from 0.5–0.6 gram of sodium and 20–30 cc. of alcohol, was then added, when the purple color appeared immediately. The bottle containing the mixture was shaken and cooled for 20 minutes (if precipitated at once, it is apt to come down in a viscous form), and then 100 to 150 cc. of ligroïn (boiling between 60° and 90°) were added, and the bottle kept cool for one hour, after which the heavy purple precipitate was removed by means of the filter pump, and thoroughly washed with ligroïn. The solid was then transferred to a platinum crucible and dried *in vacuo* over night. In the morning the substance was found partly covered with a brown crust, resulting from the decomposition of a portion of it. This was scraped off carefully, and the purple solid, which showed no signs of decomposition, dried *in vacuo* for about 40 hours in all. During the last five hours it lost less than two milligrams, and accordingly we analyzed it, as we feared it might decompose, if we attempted to dry it more thoroughly. The analyses of this preparation are given under I. and II.

It is obvious that this process could not give a pure product, unless the excess of sodic ethylate used was soluble in the mixture of ligroïn and alcohol and in the pure ligroïn. To satisfy ourselves on this point we had tried the following experiments before we carried through the preparation: Two cubic centimeters of an alcoholic solution of sodic ethylate were mixed with 30 cc. of ligroïn. No precipitate was observed. This showed that we needed not to fear the precipitation of sodic ethylate from its solution; but we felt that another experiment was advisable to determine whether sodic ethylate could be washed out of a precipitate with ligroïn.

Accordingly a concentrated alcoholic solution of dinitrobenzol mixed with a quantity of sodic ethylate was precipitated with ligroïn and thoroughly washed with this solvent. The precipitate was then ignited with sulphuric acid, when no residue of sodic sulphate was obtained. The method, therefore, is capable of giving satisfactory results.

In a second preparation of the colored compound made in the same way none of the brown decomposition-product was observed. This was dried until it lost only 0.0005 gram in three hours. The analyses of it are given under III. and IV.

I. 0.1149 gram of the substance dried *in vacuo* gave on combustion 0.1532 gram of carbonic dioxide and 0.0353 gram of water.

II. 0.3067 gram of the substance gave 0.1334 gram of sodic sulphate.

III. 0.2056 gram of the substance dried *in vacuo* gave 0.2660 gram of carbonic dioxide and 0.0660 gram of water.

IV. 0.4975 gram of the substance gave 0.2194 gram of sodic sulphate.

	Calculated for $C_6H_5OCH_3(NO_2)_2COONaNaOC_2H_5$.	I.	II.	Found.	III.	IV.
Carbon	36.15	36.37			35.28	
Hydrogen	3.01	3.41			3.56	
Sodium	13.86		14.09			14.29

A third preparation made like the preceding was dried over night *in vacuo*, when it was found that like the first it had become partially decomposed. The unaltered purple part was separated from all that had turned brown, and then dried in an air-bath at 110° to constant weight, when it was analyzed with the following results :

V. 0.3371 gram of the substance dried at 110° gave 0.1654 gram of sodic sulphate.

VI. 0.5737 gram of the substance dried at 110° gave 0.2811 gram of sodic sulphate.

	Calculated for $C_6HOCH_3(NO_2)_2COONa_2$.	V.	Found.	VI.
Sodium	16.08	15.90		15.88

According to these analyses, therefore, the substance dried *in vacuo* has lost at 110° the elements of one molecule of alco-

hol. It does not follow, however, that the loss was alcohol itself, and in this analysis during the drying we thought that we detected the odor of formaldehyde. Nor does it follow that the dried substance is closely related to the colored body dried *in vacuo*. In fact its appearance indicated that it had undergone decomposition, as it had a yellowish-brown color and did not give any purple color on the addition of absolute alcohol or of sodic ethylate. The study of this substance must be postponed till a future time.

We made a fourth preparation (as before), and studied this in the hope of determining the nature of the volatile products given off, when the purple substance is heated. This preparation was dried *in vacuo* for about 50 hours, during the last five of which it lost only 0.0012 gram. It showed no signs of decomposition, and a little of it gave a purple solution with absolute alcohol. It was then transferred to a small Erlenmeyer flask, which was connected with a flask containing a one per cent. solution of ammoniac hydrate, and a second containing a standard solution of sulphuric acid. The whole was arranged so that a stream of air purified by potassic hydrate and sulphuric acid could be drawn through the apparatus. The Erlenmeyer flask was then heated to about 100° by an oil-bath for an hour, and for a short time even to 130°. Drops of a liquid collected in the connecting-tube leading from the Erlenmeyer flask, which were driven into the ammoniac hydrate by a gentle heat. After the apparatus had cooled, the flask containing the ammoniac hydrate was stoppered tightly, and allowed to stand in a warm place over night in order that any formaldehyde present might be converted into hexamethylenetetramine. The amount of this substance formed was determined by titration, and indicated that there was a little more than one per cent. Under these circumstances we are inclined to think that no formaldehyde was present, but that this result was due to some slight experimental mistake. We could not detect the smell of formaldehyde in this or any subsequent experiment. On the other hand, the flask, when opened, exhibited a marked smell of ethyl alcohol, which was also very evident after the ammoniac hydrate had been neutralized; further a portion of this liquid

treated with iodine and potassic hydrate gave a precipitate of iodoform. We infer, therefore, that the substance given off was principally, if not entirely, ethyl alcohol. The following determinations were also made in this experiment:

0.7120 gram of the substance dried *in vacuo* lost 0.1095 gram when heated to 130°.

0.5934 gram of the salt dried at 130° gave 0.2966 gram of sodic sulphate.

	Calculated for $C_6HOCH_2(NO_2)_2COONa_2C_6H_5OH.$	Found.
Alcohol	13.86	15.38
	Calculated for $C_6HOCH_2(NO_2)_2COONa_2.$	Found.
Sodium	16.08	16.19

The per cent. of alcohol found is not so near to that calculated as we could wish, but it is sufficient to confirm the numbers in our other analyses.

The analyses given above were made with four different preparations, and show that the colored compound is formed by the addition of the elements of one molecule of sodic ethylate to one molecule of sodic dinitranisate. The bearing of our observations on the way in which the atoms are arranged in this substance has been discussed as fully as is worth while in the introduction to this paper.

In the hope of throwing more light on this part of the subject, we dissolved some of the purple body in propyl alcohol, intending to reprecipitate it by ligroïn, when the analyses of the precipitate might show whether the alcohol in the original substance was alcohol of crystallization, or more intimately united to the molecule. In the only experiment, for which we had time, the solution of the purple substance in propyl alcohol decomposed before we could reprecipitate it. The experiment will be repeated.

Decomposition of the Colored Compound from Bromdinitrobenzoic Acid.

As has been stated already, the reddish purple compound obtained by the action of sodic ethylate on bromdinitrobenzoic acid decomposed spontaneously, as was shown by the formation of sodic bromide. If this decomposition had run to

an end, as for instance when the alcohol mixed with the color was allowed to evaporate spontaneously in the air, or when the compound stood in a corked flask with alcohol for twenty-four hours, the brown product consisted principally of sodic bromide and the sodium salt of paroxydimetanitrobenzoic acid, which was recognized by the melting-point of the acid, 245° – 246° . If, on the other hand, the decomposition had not gone so far, a different product was obtained. Thus a portion of the colored compound, which had stood for some time, but still retained its reddish purple color, was treated with dilute sulphuric acid; this gave a precipitate melting at about 180° and containing halogen. Upon crystallization from very dilute alcohol this proved not to be bromdinitrobenzoic acid, as it seemed at first, but a mixture of this body with another, which, when pure, melted at 192° , and contained no bromine. Upon analysis it proved to be ethoxydinitrobenzoic acid, as shown by the following results:

0.1171 gram of the substance gave on combustion 0.1814 gram of carbonic dioxide and 0.0369 gram of water.

	Calculated for $C_8H_2OC_2H_5(NO_2)_2COOH$.	Found.
Carbon	42.19	42.24
Hydrogen	3.13	3.50

It seems, therefore, that the first products of the spontaneous decomposition of the colored compound from the bromdinitrobenzoic acid are sodic bromide and ethoxydinitrobenzoic acid, which at once combines with more of the sodic ethylate to form the colored compound derived from this acid, since the color does not change. The oxy acid is probably formed by a subsequent reaction from the ethoxy acid. Some analyses of the decomposed, but still colored, compound, showed that all the bromine had passed into sodic bromide, and that the sodium contained in the preparation not in the form of sodic bromide corresponded to that in the colored compound made from ethoxydinitrobenzoic acid.

	Calculated for $C_8H_2OC_2H_5(NO_2)_2COONaNaOC_2H_5$.	Found.	
		I.	II.
Sodium .	13.29	13.10	13.26

In other cases less satisfactory results were obtained. We

consider these numbers of but little value, because they are analyses of mixtures, but it is interesting to note that they confirm the results of the analyses of the compound from the methoxy acid given earlier in this paper.

The decomposition-products of the compound from sodic methylate and bromdinitrobenzoic acid were similar. They were sodic bromide, dinitranisic acid (paramethoxybenzoic acid), and in extreme cases oxydinitrobenzoic acid. It is possible that from both these compounds other products were formed in small quantities.

Ethoxydinitrobenzoic Acid, $C_6H_4OC_2H_5(NO_2)_2COOH$.—The method of preparing this acid by the action of sodic ethylate on bromdinitrobenzoic acid described in the last paragraph is unsatisfactory, since the yield was very small, a large part of the acid being changed during the process into the corresponding oxy acid, and also since the purification of the product was a very tedious affair. As this ethoxy acid seemed well adapted to the formation with sodic ethylate of a colored compound fit for analysis, we devoted some time to trying to find a good method for preparing it, and give here a description of one of our methods, which is of some interest, although it did not lead to the desired result. This, however, was of little importance, as in dinitranisic acid, we found a more accessible substance as well adapted to our purpose.

This method was founded on the hope that the ethylester of ethoxydinitrobenzoic acid might be made by the violent action of hydrochloric acid on an alcoholic solution of chrysanic ester (amidodinitrobenzoic ester), the amido group being replaced by the ethoxy radical, and ammoniac chloride being formed. Accordingly the alcoholic solution of this ester saturated with hydrochloric acid in the cold was heated to 100° in a sealed tube for five hours. The residue, after the liquid had been evaporated off, was crystallized from ligroin, which finally gave a substance melting at 114° , and was, therefore, unaltered chrysanic ester. The first mother-liquors were allowed to evaporate spontaneously, when they deposited, in addition to the yellow crystals of chrysanic ester, others which were colorless, long, obliquely terminated prisms; these were separated mechanically, and found to melt at 60° . Sal-

kowski gives the melting-point of ethoxydinitrobenzoic ethylester as 59° . The crystals also gave with sodic ethylate the rose-pink color obtained from this reagent, and the bromdinitrobenzoic ethylester. We feel no doubt, therefore, that we obtained the ethylester of ethoxydinitrobenzoic acid by the action of hydrochloric acid and alcohol on chrysanic acid, but as the yield was very small, the method is of no practical value.

Properties. — The ethoxydinitrobenzoic acid crystallizes from alcohol in long, flat, colorless prisms, terminated by a single plane at an oblique angle. It takes on a faint yellow tinge when exposed for some time to the air. It melts at 192° . It is very soluble in ether, acetone, or ethyl acetate; easily soluble in benzol, or glacial acetic acid; moderately soluble in chloroform, or carbonic disulphide; fairly soluble in cold ethyl or methyl alcohol, more soluble in either of these solvents, when hot; slightly soluble in cold water or ligroin, more soluble in either, if hot. The best solvent for it is alcohol. Slightly soluble in hot, strong hydrochloric acid; soluble in strong sulphuric acid, or nitric acid. It is soluble in solutions of alkalies, or alkaline carbonates forming its salts. A solution of the sodium salt prepared by adding the proper amount of sodic carbonate to a weighed portion of the acid gave the following characteristic reactions:

Argentie nitrate or *ferrie chloride*, white precipitate.

Cupric sulphate, light green, slightly soluble precipitate.

Plumbic acetate, white precipitate, slightly soluble in cold, freely soluble in hot water.

Baric chloride, white precipitate, soluble with tolerable ease.

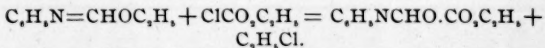
The sodium salt itself crystallizes in easily soluble yellow needles. The ethoxydinitrobenzoic acid is not a very stable substance, as dilute acids, or alkalies convert it when warmed into oxydinitrobenzoic acid. Ammonic hydrate gives chrysanic acid with it. The reddish purple compound with sodic ethylate has been already described.

XLIX.—ON THE ACTION OF CHLORCARBONIC ETHYL ESTER ON FORMANILIDE.

BY H. L. WHEELER AND H. F. METCALF.

Sixteen years ago Lellmann¹ made the interesting observation that chlorcarbonic ethyl ester reacts energetically with formanilide, while with acet- or benzanilide no reaction was obtained, even on heating under pressure. Lellman isolated and identified diphenylformamidine as one of the products of the reaction. He explained the formation of the amidine by stating that perhaps formylphenylurethane is formed, and that this compound appears to be quite unstable, two molecules breaking up into the amidine, carbon dioxide and ethyl oxalate.

Formylphenylurethane has been prepared by us by the action of chlorcarbonic ethyl ester on phenylimidoethyl formate or ethylisoformanilide. The reaction is precisely similar to the action of other acid chlorides on the isoanilides, and it takes place as follows: ²



The products being formylphenylurethane and ethyl chloride. Thus prepared it is an oil which can be distilled with little or no decomposition. It is no more unstable than other mixed diacid anilides, and it does not suffer the above mentioned decomposition. When warmed with acid or alkali, the formyl group is removed and phenylurethane results. It will be shown below that no ethyl oxalate is formed in the action of chlorcarbonic ethyl ester on formanilide, and that therefore Lellmann's explanation is incorrect.

Just recently Freer and Sherman³ have undertaken a re-examination of this reaction. They isolated the amidine, and state that in addition to this they obtained an oil which was washed with water, and which would not solidify, while "after slight warming it broke down, giving off a gas and changing to diphenylformamidine, thus showing conclusively,

¹ Ber. d. chem. Ges., 14, 2512.

² This JOURNAL, 19, 129.

³ This JOURNAL, 18, 579.

according to Wheeler,¹ that it was ethylisoformanilide, $C_8H_9N=CHOC_2H_5$."

If Freer and Sherman had examined the oil more carefully, which is obtained according to their directions, they would have found that it is not ethylisoformanilide. Moreover, it does not contain the slightest trace of this compound. The properties of the oil and the fact that it even partially withstood the treatment it received, show conclusively that it was not ethylisoformanilide. Ethylisoformanilide or phenylimidoethyl formate was first obtained by Comstock and Clapp.² These authors describe it, as stated in Beilstein's Handbuch,³ as an oil boiling from 213° to 215° at 741 mm. pressure.⁴ In the article to which Freer and Sherman refer this imido ester was not described as an oil which decomposes on distillation, but which boils at 18 mm. pressure at about 106° . Under these conditions it has therefore almost the same boiling-point as its isomeric imido ester, *i. e.*, imido ethyl benzoate.⁵

Ethylisoformanilide and all the other isoanilides prepared in this laboratory⁶ differ from the imido esters of Pinner, inasmuch as they cannot be washed with water without decomposition; indeed, on exposure to the moisture of the air, they soon solidify, changing into the corresponding amidines, or regenerating the formyl compound. The peculiar penetrating pleasant odor of the isoanilides, like that of the imidoesters of Pinner, is characteristic and traces of these compounds can readily be detected by their odor. This odor was entirely lacking in the above mentioned oil.

If ethylisoformanilide is formed in the action of chlorcarbonic ester on formanilide, which most probably is the first step of the reaction, its existence would naturally be very brief in the presence of chlorcarbonic ester, and, as shown in this paper, it would further react, not only with the chlorcarbonic ester, giving formylphenylurethane, but also probably with hydrogen chloride and the water, which are formed as by-products.

From this and the following it will be seen that hitherto the only products which have been accurately identified in this

¹ This JOURNAL, 18, 381.

² *Ibid.*, 13, 527.

³ Dritte Auflage, p. 359.

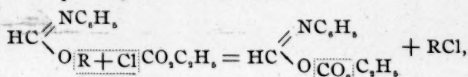
⁴ Compare also Claisen: Ann. Chem. (Liebig), 287, 364.

⁵ Bushong: This JOURNAL, 18, 490.

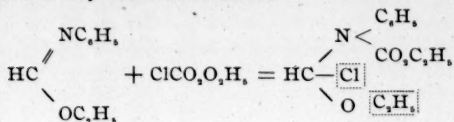
⁶ *Ibid.*, 12, 499; 13, 515, 525.

reaction are diphenylformamidine hydrochloride and carbon dioxide. By a more thorough examination of this reaction we have obtained the following as final reaction-products: Diphenylformamidine hydrochloride, formylphenylurethane phenylurethane, carbon dioxide, carbon monoxide and ethyl chloride, and the oil which Freer and Sherman state is ethyl-isoformanilide will be shown in the experimental part of this paper to be a mixture of the nitrogen derivative formphenylurethane, phenylurethane, and any unaltered formanilide. It must also have contained some chlorcarbonic ester when they attempted the distillation. It frequently has a slight odor resembling monochlorethylacetate, which possibly comes from a slight impurity in the carbonic ester. At any rate the quantity of this material is extremely small.

The formation of the above products would seem to indicate that formanilide and silver formanilide react with chlorcarbonic ethyl ester in the same manner, except that in the case of formanilide the reaction is complicated by the secondary reactions of hydrogen chloride. The products in these two reactions are identical, so that one general equation may represent the primary reaction as follows:



the unstable isodiacid anilide thus formed separating carbon dioxide, which is frequently the case with chlorcarbonic ester reactions, giving phenylimidoethyl formate. Here, however, it has only a brief existence, as it immediately reacts with the chlorcarbonic ester, giving formylphenylurethane and ethyl chloride as follows:¹

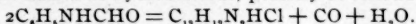


¹ In the case of the silver salt a small amount of ethylisoformanilide was actually isolated. It is therefore evident that the chlorcarbonic ester has a greater tendency to react with the silver salt than with the isoanilide, while in the case of formanilide the facts are the reverse.

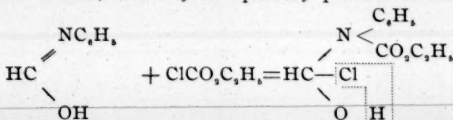
On the other hand, the ingenious suggestion of Freer and Sherman to account for the formation of ethylisoformanilide, may represent the primary course of the reaction if formanilide has the structure $\text{HC}-\text{NHC}_6\text{H}_5$. They assume that the

O
chlorcarbonic ethyl ester adds on the nitrogen, which then becomes pentavalent, and the addition-product thus formed decomposes into the imido ester, carbon dioxide and hydrogen chloride. It is to be noticed that if the reaction takes place in this manner, it is analogous to the action of other acid chlorides on the anilides, at least in regard to the formation of an intermediate pentavalent nitrogen addition-product.¹

At any rate, there is little doubt that phenylimidoethyl formate is the first product of the reaction. Wallach² has shown that hydrogen chloride converts formanilide into diphenylformamidine hydrochloride, possibly as follows:



This and the fact that the isoanilides are converted into amidines by hydrogen chloride³ accounts for the formation of carbon monoxide and the amidine hydrochloride in the above reaction. The formation of carbon monoxide may also be due to the displacement of the formyl group, as formyl chloride, which decomposes into the oxide and hydrogen chloride.⁴ Formylphenylurethane may be a secondary product and result from the action of the chlorcarbonic ester on the isoanilide first formed, or it may be a primary product as follows:



its formation then being analogous to that of the diacid anilides from the silver salts⁵ and from the isoanilides⁶. Phenylurethane naturally results from formylphenylurethane, since all mixed diacid anilides, by treatment with acids, first liberate the lower acid radical.

¹ Pictet: Ber. d. chem. Ges., 23, 3015.

² Ibid, 15, 208.

³ Comstock and Kleeburg: This JOURNAL, 12, 493.

⁴ Compare Pictet: Loc. cit.

⁵ Wheeler and Boltwood: This JOURNAL, 18, 381.

⁶ Wheeler and Walden: Ibid, 19, 129.

Thus it will be seen that the formation of all the products of the action of chlorcarbonic ethyl ester on formanilide can readily be explained whether formanilide, as its name implies, is an anilide with the structure $\text{HCO.NHC}_6\text{H}_5$, or whether it has the imido structure and is phenylimidoformic acid. Its structure cannot, therefore, be determined by the final reaction-products in this case, but the analogy which this reaction shows with that of the silver salt is strongly in favor of the imido formula.

The recent work bearing on the structure of formanilide appears to favor the view that this compound is an imido acid. Cohen and Archdeacon¹ conclude from their interesting work on sodium alcoholate addition-products of the anilides, that the structure of formanilide and indeed also of other anilides is best represented by the imido formula.

Claisen,² on the other hand, has recently given what at first sight appears to be a strong argument for the amide structure, *i. e.*, that the sodium salts of the true oxymethylene compound, oxymethylene camphor, for example, give O-esters with ethyl iodide, while formanilide does not. He carries, however, this analogy, or lack of analogy, too far when he states that if formanilide has the structure $\text{C}_6\text{H}_5\text{N}=\text{CHOH}$, it should boil lower than its O-ethyl derivative, $\text{C}_6\text{H}_5\text{N}=\text{CHOC}_2\text{H}_5$, while the fact is that formanilide boils higher.

He arrived at this conclusion from a consideration of the boiling-points of the following compounds:

	B. P.	B. P.
Oxymethylene camphor	251°	O-Ethyl derivative 270°
Oxymethylene-acetoacetic ester	200°	O-Ethyl derivative 266°
Oxymethylene-acetylacetone	190°-200°	O-Ethyl derivative 257°

The objection to this reasoning is that the above compounds do not contain the nitrogen-carbon grouping $\text{—N}=\text{CHOH}$ in question, but the carbon-carbon grouping $\text{=C}=\text{CHOH}$, which is assumed to be analogous without sufficient reason. For it might be argued that compounds containing the nitrogen-carbon grouping $\text{—N}=\text{CHOH}$ would show differences in the boiling-points similar to those containing the oxygen-carbon grouping $\text{O}=\text{CHOH}$, that is that the imido acids and their esters would

¹ J. Chem. Soc. (1896), 91.

² Ann. Chem. (Liebig), 287, 360.

be expected to correspond with the simple acids and their esters, and, since the acids boil higher than their esters and formanilide higher than its ester, the structure $C_6H_5N=CHOH$ is the correct one for formanilide.

For example:

	B. P.		B. P.
$O=CHOH$	99°	$O=CHOC_2H_5$	54°.4
$O=C(CH_3)OH$	118°	$O=C(CH_3)OC_2H_5$	77°
$O=C(C_2H_5)OH$	250°	$O=C(C_2H_5)OC_2H_5$	213°
$C_6H_5N=CHOH$	294°	$C_6H_5N=CHOC_2H_5$	212°

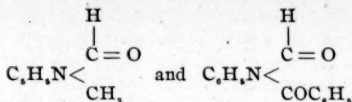
Similar reasoning to that which has led Claisen to consider formanilide as an anilide may be employed to show that it is not. For if instead of drawing conclusions in regard to its structure from comparison of compounds containing the group $=C=CHOH$ with their ethyl esters, a comparison is made of compounds containing the group $\equiv C-CHO$, with what theoretically would be their O-derivatives, we find that the compounds with the true formyl group, in this case also, boil lower than the O-ethyl derivatives. Therefore, since the boiling-point of formanilide does not correspond with this series, formanilide must have the imido structure.

For example:

	B. P.		B. P.
$H_2C=CHO$	20°.8	$H_2C=CHO-C_2H_5$	35°.5
$(CH_3)_2CO=CHO$	63°	$(CH_3)_2C=CHOC_2H_5$	92°-94°
$CH_3(C_2H_5)CH=CHO$	90°	$CH_3(C_2H_5)C=CHOC_2H_5$	111°
$C_6H_5NH=CHO$	294°	$C_6H_5N=CHOC_2H_5$	212°

This shows that there is no analogy to be expected between the boiling-points of oxymethylene derivatives containing the group $=C=CHOH$ with formanilide. On account of the relation which exists between the boiling-points of acids and their esters, and since formanilide or phenylimidoformic acid and its ester show this same relation, the conclusion to be drawn (if any) from the boiling-points is that formanilide has the imido structure.

Although the group $-N=CHOH$ may exist in formanilide, it cannot exist in the secondary anilides, that is, in such compounds as methyl formanilide, or in the diacid anilides, benzoyl formanilide, for example. These compounds must have the structure,



Auwers¹ has found that formanilide shows in its cryoscopic behavior a departure from the formyl secondary anilides. This, as Auwers states, may be due to some unknown cause, and not necessarily result from the presence of hydroxyl in formanilide.

It is interesting also to note that formanilide as first shown by Comstock and Kleeburg, readily forms a silver salt, while acet- and benzanilide apparently do not. It may be stated in general that formanilide is far more reactive than the other anilides. These facts would seem to indicate that formanilide has the imido structure, and therefore reacts with chlorcarbonic ethyl ester in the manner first stated above.

EXPERIMENTAL PART.

Action of Chlorcarbonic Ethyl Ester on Formanilide.

On mixing chlorcarbonic ethyl ester and formanilide, an absorption of heat takes place, the formanilide slowly dissolves, and, at 23°, a slow evolution of gas soon takes place. At 60° to 70° the evolution of gas is rapid, while on the water-bath it may become violent, as Lellmann observed.

The Liquid and Solid Products.—60 grams of formanilide and 54 grams of chlorcarbonic ethyl ester were mixed and warmed until solution took place, and the reaction was well started. After a short time the material was placed in a desiccator over lime until the odor of the ester had disappeared. It was then taken up in ether and separated from the diphenylformamidine hydrochloride which remained. This residue was dissolved in water and precipitated by ammonia, when it melted at about 136°. The ethereal solution was washed with water, until all the amidine salt was removed; it was then dried over calcium chloride and the ether evaporated. This then gave the oil which has been stated contains ethyl oxalate and ethylisoformanilide. A portion of this was shaken with strong ammonia; it then showed no signs of

¹ Ztschr. phys. Chem., 12, 711; and 15, 43, 49.

alteration and no oxamide was obtained. Ethyl oxalate could not, therefore, have been present. Another portion was shaken with dilute hydrochloric acid; the remaining oil was extracted with ether and the aqueous acid solution was then found to contain nothing but a trace of aniline hydrochloride. Since no amidine was formed by this treatment, the absence of ethylisoformanilide in this oil is established. The remaining portion of the oil, which had not been treated with ammonia or acid, and which had a slight odor resembling monochlorethyl acetate, but none resembling ethylisoformanilide, was then subjected to distillation. Unsuccessful attempts were previously made to solidify this oil by freezing. On distilling, it all boiled over at 14 mm. pressure from 159° to 165° without showing any signs of decomposition, at least the amount of gas given off, as stated by Freer and Sherman, was so insignificant that the pressure remained constant during the entire distillation. The residue was also insignificant and diphenylformamidine was not formed. The oil was again distilled at 15 mm. pressure. It then boiled for the greater part from 162° to 164°. On further distilling it showed signs of decomposition, the boiling-point rose to 170°, and in the receiver a trace of a sharp odor, probably of phenyl isocyanate, was noticed. The distillate remained as an oil on cooling. It was then boiled with sodium hydroxide in dilute alcoholic solution, in order to decompose formylphenylurethane into phenylurethane. On cooling, an oil separated, which when treated with dilute hydrochloric acid, solidified in a freezing-mixture. On crystallizing this material from dilute alcohol, it melted at 52°, and in all its properties was identical with phenylurethane.

Phenylurethane is one of those substances which when melted, or when separated from an alcoholic solution, may remain liquid for a long time. Formanilide also belongs to this class of substances which when impure are difficult to solidify, while formylphenylurethane is an oil. Mixtures of the above substances would not therefore be expected to completely solidify or readily to deposit crystals on cooling.

In another experiment where the action was more complete and no formanilide apparently was present, a portion of the

oil did solidify on cooling, and this was found to be phenylurethane. On boiling the whole with sodium hydroxide, and then cooling, it apparently solidified completely, giving only the urethane. This shows that the oil was undoubtedly mostly formylphenylurethane, and the oil which Freer and Sherman obtained must have contained the above mentioned substances along with some chlorcarbonic ester, since they state that on warming it gave off a gas, and they obtained more amidine, that is, in their case, the reaction was not completed at first.

In another experiment, using two molecules of formanilide to one of chlorcarbonic ethyl ester, the products were the same. Hence naturally the oil contained a large amount of formanilide. The greater portion of this was separated by concentrating the ethereal solution when the formanilide separated as an oil, which on standing crystallized. The ethereal filtrate from this gave an oil which boiled for the most part at 14 mm. pressure from 147° to 151° . The observed boiling-point of formylphenylurethane in the same apparatus at 15 mm. pressure was 149° to 151° , while phenylurethane boiled at 151° , and formanilide at 165° – 166° . Since in the above reaction hydrogen chloride is formed, and this converts the formylphenylurethane into phenylurethane, the oil is therefore always a mixture of these compounds, and it contains in addition any unaltered formanilide. Since the boiling-points of these substances lie so closely together, attempts to isolate formylphenylurethane, free from admixture, in this case were abandoned. The oil was then converted into the urethane by boiling with sodium hydroxide, and the product thus obtained was a mixture of urethane and formanilide.

Formanilide and phenylurethane in the absence of formylphenylurethane, *i. e.*, after boiling with sodium hydroxide, etc., can readily be separated. When such a mixture is crystallized from quite dilute alcohol, formanilide first separates, while when the mixture is treated with ligroin it is the phenylurethane that is extracted.

A better yield of the oil can be obtained by carrying out the reaction in benzene.

The Gaseous Products.—The gases were collected over

water and examined as follows: The carbonic acid and ethyl chloride were removed together with cold dilute solution of sodium hydrate; the presence of carbon dioxide was then shown in the usual way. On warming this solution ethyl chloride was given off. This burned with a greenish flame, and was shown to contain chlorine by passing the gas over heated calcium oxide, dissolving in nitric acid and precipitating with silver nitrate. Separate experiments under the same conditions with chlorcarbonic ester and boiling sodium hydrate gave no burnable gas. Carbon dioxide and ethyl chloride are the chief constituents of the gaseous products. After the sodium hydrate solution and then cold water failed to diminish the volume of gas, a cuprous chloride solution in hydrochloric acid was run into the burette. This absorbed the greater part of the remaining gas, thus showing the presence of carbon monoxide, the comparatively small part not absorbed was air which had accidentally entered in handling the products.

The results of the above experiments serve to identify the following compounds: Diphenylformamidine hydrochloride, formylphenylurethane, phenylurethane, carbon dioxide, carbon monoxide and ethyl chloride.

Formylphenylurethane, $C_6H_5N < \begin{matrix} CHO \\ CO_2C_2H_5 \end{matrix}$.—This diacid es-

ter anilide was not obtained free from formanilide or phenylurethane when chlorcarbonic ethyl ester acted on formanilide. It can be obtained pure, however, from ethylisoformanilide and chlorcarbonic ethyl ester as follows:

16 grams of ethylisoformanilide were treated with a slight excess, over one molecule of the ester, a lively reaction took place (requiring the use of a return-condenser). Heat was evolved and a stream of ethyl chloride escaped. The reaction was complete in a short time. The whole was then placed over lime in a desiccator until the odor of chlorcarbonic ester disappeared. It was then distilled, and after fractioning, a portion was obtained boiling from 149° to 151° at 15 mm. pressure. This did not solidify on cooling, and on analysis the following results were obtained:

	Found.	Calculated for $C_{10}H_{11}NO_3$.
C	62.67	62.18
H	5.98	5.69
N	7.55	7.23

When the analyzed material was boiled with alkali it decomposed with the separation of the lower acid group, giving phenylurethane. When it was mixed with phenylhydrazine, it soon solidified; the solid was washed with ether, and this then left pure α -formylphenylhydrazine, melting at 140° . These results show that formylphenylurethane has the structure above assigned to it, both acid groups being attached to nitrogen.

NEW HAVEN, DEC., 1896.

NOTES OF STUDENT WORK FROM THE LABORATORY OF ANALYTICAL CHEMISTRY, UNIVERSITY OF VIRGINIA.

COMMUNICATED BY F. P. DUNNINGTON.

XX.

162.—DRYING AND DELIQUESCENT OF CERTAIN SALTS.

BY F. W. SMITHER.

Having in view the selection of a substance which is well adapted to use as an absorber of water in an hygrometer, these several salts were chosen as not prone to corrode organic matter or to decompose upon prolonged exposure to a dry or moist atmosphere, and it was proposed to make some determinations of their relative power of absorbing and retaining moisture.

Shortly after having begun this work I saw a notice of a paper by Dr. H. Wilson Hake, read before the Chemical Society of London, Feb. 6, 1896, upon "The Absorption of Moisture by Deliquescent Salts," but, inasmuch as I had then already observed larger absorption of water than was there noted, these results suggested the propriety of continuing this investigation for a greater length of time, aiming thus to ascertain what limits, if any, exist in the absorption of water by such substances.

Each of the salts employed was made from the correspond-

ing carbonate and the amount present was determined in the form of sulphate from similar portions of the solutions used.

Drying of Certain Salts.

In order to ascertain the amount of water retained by these salts when dried in a steam-bath: A definite portion of each was placed in a weighed beaker of about 100 cc. capacity, together with 20 grams of coarsely powdered glass. The glass sufficed to absorb the solution and so secure a better exposure of the salt. These were then dried in a steam-bath at a temperature of 97-98° C., and thus heated for from six to eight hours, cooled, and weighed, kept in a desiccator over night, and re-heated the next day. The daily heating of these salts was continued until the changes which took place appeared well defined. The weights are shown in Table A.

Table A.

Salts anhydrous.	Residues left upon drying.				
	LiCl. 0.2135	CaCl ₂ . 0.2864	CaN ₂ O ₄ . 0.4349	MgCl ₂ . 0.1907	MgN ₂ O ₄ . 0.3840.
After 1st day	0.2250	0.3758	0.5087	0.2693	0.4791
" 2nd "	0.2212	0.3605	0.5053	0.2649	0.4547
" 3rd "	0.2212	0.3531	0.4908	0.2579	0.4500
" 4th "	0.2212	0.3252	0.4807	0.2527	0.4411
" 5th "	0.2162	0.3214	0.4727	0.2499	0.4317
6-10 "	0.2171	0.3372	0.4862	0.2471	0.4380
11-15 "	0.2121	0.3210	0.4758	0.2345	0.4104
16-20 "	0.2128	0.3186	0.4654	0.2274	0.3929
21-25 "	0.2148	0.3265	0.4648	0.2228	0.3858
26-30 "	0.2155	0.3244	0.4626	0.2184	0.3689
30th "	0.2132	0.3200	0.4550	0.2136	0.3458

After the 5th, I have for brevity given only the average weight for each five days, sufficing to show the very slow rate at which some of the water is to be removed. In the latter portion of this experiment the salts of magnesia had lost acid to a small extent, as was indicated by the separation of a white insoluble crust of magnesium hydrate, the amount of which was estimated at the close. Many years ago it was observed that these magnesium salts could not be rendered anhydrous without this decomposition.

The considerable surface of glass exposed in obtaining these weighing will account for a slight variation in the

weights and toward the close of the experiment, no doubt, some water was re-absorbed each night from the calcium chloride of the desiccator. Therefore, a few of the weights which appeared decidedly inaccurate were omitted in making up the averages given.

From this work the following observation may be made :

Lithium chloride is soon rendered anhydrous and is unaltered upon further heating in the steam-bath, but it is exceedingly hygroscopic at common temperatures.

Calcium chloride, upon the fifth heating, retained less than 1 molecule of water, and thereafter it lost and regained a small fraction of this repeatedly.

Calcium nitrate, upon the fourth heating, retained 1 molecule of water and subsequently it gave up a portion of this very slowly.

Magnesium chloride, upon the second heating retained 2, and upon the nineteenth retained 1 molecule of water, beyond this point it gradually lost acid.

Magnesium nitrate, upon the first heating, retained 2, upon the eighth, 1 molecule of water, and thereafter gradually lost water and a little acid forming some magnesium hydrate as above.

The Absorption of Water.

A similar set of beakers were filled with similar amounts of the several salts used above. In each of these was placed a piece of flat cotton lamp-wick of about two square inches, which sufficed to absorb the solution and afford a greater exposure of the salt. The beakers were placed under a bell-jar of 12 gallons capacity, the atmosphere of which was charged with water from 2 flat dishes, exposing 57 square inches surface of water. Subsequently, a number of estimations were made of the dew-point of the atmosphere within this jar after standing twenty-four hours, which proved to be from 2.0 to 3.5° C. below the temperature.

Each day, when the weighings were made, the atmosphere within the jar was replaced by that of the room, so that for a portion of each day these salts were exposed to the dryer atmosphere of the room.

These experiments were conducted in a protected room,

where the temperature varied but little from day to day. The temperature at the time of weighing is given in the table.

The absorptions for the first day were observed upon the specimens which had been long dried at 97° C. upon glass, of which the magnesium salts were in small measure decomposed as stated above.

All the remaining observations of this series were made upon similar portions of the same salts, perfectly neutral, absorbed upon cotton-wick, and brought to the degree of moisture at which the previous samples were substituted.

There was an unimportant inaccuracy in respect to the time, in that there were but six days in the seventh "week," and but five in the eighth "week."

These beakers containing the salts were weighed almost daily for seven weeks, and thereafter weekly, and the weights of water absorbed are indicated in Table B.

Table B.

Salts Anhydrous Water retained	Amounts of water absorbed.					Temp. °C.
	LiCl. 0.2135 0.0000	CaCl ₂ . 0.2864 0.0336	CaN ₂ O ₄ . 0.4349 0.0201	MgCl ₂ . 0.1907 0.0229	MgN ₂ O ₄ . 0.3840 0.0277	
After 2 hours	0.063	0.128	0.093	0.100	0.111	19
" 4 "	0.101	0.173	0.127	0.138	0.134	20
" 6 "	0.137	0.210	0.163	0.159	0.157	20
" 8 "	0.176	0.243	0.193	0.178	0.176	22
" 10 "	0.206	0.268	0.216	0.204	0.192	23
" 24 "	0.451	0.519	0.366	0.332	0.335	25
" 2 days	0.750	0.721	0.533	0.544	0.704	20
" 3 "	0.923	0.876	0.642	0.641	0.848	20
" 4 "	1.079	0.997	0.750	0.731	0.978	20
" 5 "	1.195	1.092	0.828	0.792	1.073	23
" 6 "	1.300	1.165	0.892	0.847	1.139	25
" 7 "	1.409	1.206	0.923	0.893	1.170	23
" 2 weeks	2.095	1.540	1.246	1.490	1.521	20
" 3 "	2.495	1.868	1.554	1.682	1.828	20.5
" 4 "	2.647	1.919	1.637	1.667	1.931	17
" 5 "	2.713	1.875	1.658	1.594	1.968	17.5
" 6 "	2.717	1.783	1.624	1.481	1.951	17.5
" 7 "	2.782	1.817	1.662	1.494	1.995	18
" 8 "	2.888	1.876	1.743	1.626	2.029	20.5
" 9 "	3.098	1.994	1.883	1.630	2.205	15.5
" 10 "	3.186	1.966	1.916	1.659	2.262	14.5
" 11 "	3.269	1.994	1.940	1.664	2.301	16
" 12 "	3.327	2.127	2.055	1.778	2.463	12

It appears that when the atmosphere is nearly saturated with moisture, these salts continue to absorb water, and most conspicuously, lithium chloride takes up more than fifteen times its weight. During the sixth week the lithium chloride ceased to absorb and the other salt lost water. I can only explain this by the possibility of the water supply under the bell-jar becoming exhausted. Water was added from time to time, but it was never noticed to have thus dried up.

The amounts of water absorbed are thus found to be far in excess of the figures reported by Dr. Hake in the article above referred to. In each case the water taken up in one week was not half of what was absorbed in the subsequent eleven weeks.

As to the formation of any definite hydrate, the number of molecules of water present at each observation has been calculated in Table C. For the sake of uniformity in valency, the calculations are made for a double molecule of lithium chloride.

Table C.

Molecular weight	Molecules of water absorbed by one molecule of each salt.				
	Li_2Cl_2 85.	CaCl_2 111.	CaN_2O_4 164.	MgCl_2 95.	MgN_2O_4 148.
Water at beginning	0.00	0.72	0.42	0.63	0.59
After 2 hours	1.39	2.72	1.95	2.76	2.37
" 4 "	2.23	3.72	2.66	3.82	2.86
" 6 "	3.03	4.53	3.41	4.41	3.36
" 8 "	3.89	5.24	4.05	4.93	3.67
" 10 "	4.57	5.77	4.53	5.64	4.10
" 24 "	9.98	11.15	7.67	9.16	7.16
" 2 days	16.60	15.54	11.16	14.98	15.07
" 3 "	20.41	18.88	13.45	17.75	18.15
" 4 "	23.86	21.48	15.71	20.24	20.94
" 5 "	26.43	23.44	17.35	21.93	22.97
" 6 "	28.75	25.10	18.69	23.43	24.39
" 7 "	31.15	26.00	19.33	24.71	25.05
" 2 weeks	46.25	33.19	26.11	41.25	32.56
" 3 "	55.19	40.27	32.56	46.54	39.14
" 4 "	58.55	41.27	34.30	46.13	41.35
" 5 "	60.02	40.40	34.74	44.12	42.14
" 6 "	60.11	38.43	34.02	40.98	41.77
" 7 "	61.43	39.14	34.83	41.34	42.71
" 8 "	63.88	40.42	36.52	45.00	43.44

Molecular weight.	Molecules of water absorbed by one molecule of each salt.				
	Li_2Cl_2 85.	CaCl_2 111.	CaN_2O_3 164.	MgCl_2 95.	MgN_2O_4 148.
After 9 weeks	68.52	42.98	39.45	45.11	47.20
" 10 "	70.46	42.26	40.14	45.91	48.44
" 11 "	72.33	42.97	40.65	46.06	49.24
" 12 "	73.60	45.82	43.15	49.20	52.72

An examination of these results exhibits no defined cessation in absorption, unless there is a tendency for calcium chloride to form a hydrate with 40 molecules of water. Hence it must be admitted that if any definite hydration in the solution takes place, such combination is so feeble that it would require a carefully maintained temperature and degree of humidity in the surrounding atmosphere to render it possible of recognition. And it is concluded that these salts do not form any hydrates when in the liquid state, at common temperature.

163.—ANALYSIS OF A VARIETY OF ILMENITE.

BY GEORGE M. FEEK.

This mineral, received from Dr. Thos. K. Terrell, of Lynchburg, is found in Bedford Co., Va., about one mile from Forest Depot, N. & W. R. R. It occurs enclosed in a vein of quartz, in plates 1 cm. or more in thickness, cleaves well in one direction and less readily in another, at an angle of 45° ; crystallization probably tetragonal, brittle, hardness = 5.25, not magnetic, sp. gr. = 4.699, fusibility = 5, and upon analysis presents the following composition:

		Molecular ratio.
TiO_2	63.31	3.16
FeO	35.99	2.00
MgO	0.82	0.16
SiO_2	1.25	
	101.37	

This composition affords approximately the formula $2(\text{FeO}), 3(\text{TiO}_2)$, or $\text{Fe}_3\text{Ti}_3\text{O}_{11}$, which lies between that of typical Ilmenite $2(\text{FeO}), 2(\text{TiO}_2)$, and that of Iserite (Janovsky) : $2(\text{FeO}), 4(\text{TiO}_2)$.

164.—"MINERAL TALLOW" FROM DANBY, VERMONT.

BY L. E. SMOOT.

Through the kindness of Mr. J. J. Cochrane, of Dorset, Vt., a specimen of this substance has been received. In a limestone cavern near Danby and about 12 miles from Rutland, Vt., this peculiar deposit is found on the walls, in a layer 2 or 3 inches in thickness. It is of a soft, smooth, putty-like consistency, nearly white, and an occasional slight increase in admixed dust shows that it has been formed in layers, each 1 or 2 mm. thick. When allowed to dry, it hardens to a pith-like mass, but upon being again moistened, resumes its original consistency. Under a magnifying power of 412 diameters, it exhibits no crystallization, but is seen as an aggregation of exceedingly minute rod-like particles, suggesting some forms of bacteria, and with this there are some thin films of irregular rounded shapes affording colors (of thin films). When heated in a closed tube, it chars and affords a small amount of alkaline vapors.

An analysis of the clean, white portion by Mr. Smoot shows the following composition:

		Dried.
Lime	7.63	52.19
Magnesia	0.04	0.27
Carbon dioxide	6.04	41.31
Silica	0.52	3.57
Water, lost in desiccator	84.37	
" " at 130° C.	1.01	
Organic matter (by diff.)	0.39	2.66
Nitrogen		(0.053)
	100.00	100.00

The absence of crystallization suggests that this small portion of organic matter takes an important part in determining the nature of the deposit. The proportion of mineral matter does not greatly differ from that secreted by the oyster, in which the average per cent. of organic matter constitutes but 2.39 of the total dry matter, against 2.66 in the present instance. The amount of nitrogen is smaller, but this would naturally be the first element to be lost upon decomposition of organic matter. Probably, therefore, this large amount of calcium carbonate has been secreted by some minute form of life.

165.—ANALYSIS OF DOLOMITIC MARBLE FROM TEXAS, MD.

BY GEORGE G. BUCK.

For many years this marble has been extensively quarried and is specially valued by reason of its uniform compactness and hardness above that of most other marble.

An average sample taken from the stone employed in building the depot at Glyndon, W. Md. R. R., affords the following results. It has a faint yellow tint, hardness = 3.5, sp. gr. = 2.865, and its composition is :

		Molecular ratio.
Lime	31.58	8.02
Magnesia	19.64	7.04
Ferrous oxide	0.14	0.03
Carbon dioxide	47.55	15.44
Silica	1.27	
	100.18	

Which result shows that it approximates fairly to a true dolomite.

156.—ANALYSIS OF AN ALUM WATER FROM LEE CO., VA.

BY L. E. SMOOT.

This water is from a spring on the farm of Dr. J. E. Browning, 9 miles north-west of Jonesville, Lee Co., Va. It is odorless, colorless, with a decided acid reaction and strong alum taste. Temperature at spring, 70° F. Upon analysis it is found to contain in 1 liter :

	Gram.
Alumina	0.891
Ferric oxide	0.120
Soda (and trace potash)	0.060
Sulphuric oxide	2.530
Nitric acid	0.006
Silica	0.108
	3.715

From which we calculate. One pint contains

	Grains.
Aluminum sulphate	21.805
Ferric sulphate	2.190
Sodium sulphate	1.015
Sulphuric acid, free	1.598
Nitric acid	0.050
Silica	0.788

 27.446

This peculiarly large amount of aluminum sulphate seems worthy of note. This water is about twice the strength of the strongest alum water of Stribling Springs, Augusta Co., Va., which in other respects it much resembles.

 167.—ANALYSES OF INFUSORIAL EARTH.

BY F. W. SMITHER.

On the northern bank of the Rappahannock river, at Greenlaw's wharf, in King George Co., Va., there is a bank of Tripolite about 30 feet in thickness, most of which is of a light-brown color and some of it is almost pure white. A specimen of the latter was examined and appeared under the microscope to consist almost exclusively of perfect infusorial shells containing comparatively little of fragments and extraneous matter. For this reason it was thought well to make an analysis of it.

In connection with this an analysis was also made of a specimen from a similar bank of Tripolite on the Patuxent River, in Calvert Co., near Anne Arundel Co., Md., which is of a pale gray color and consists largely of perfect infusorial shells.

A similar examination was also made of the earth from the well-known bed in Richmond, Va. The sample taken from President's Hill is of a light-brown color.

These three deposits lie in a line running north-east from Richmond and about 40 miles apart.

In the endeavor to estimate the proportion of the infusorial shells it was found that a 30 per cent. solution of sodium hydrate, at 100° C., required about two hours to remove all the shells. A 20 per cent. solution did not dissolve all in six hours. In each case the solvent was allowed to act until,

upon examination with the microscope, infusorial shells were no longer to be seen.

Analyses of these specimens afforded:

	Rappahan- nock.	Rich- mond.	Patux- ent.
Silicon, amorphous	65.83	51.67	48.58
Silica, crystallized	14.65	23.56	35.23
Titanic oxide	0.40	0.64	0.60
Ferric oxide	2.34	2.79	1.20
Alumina	4.17	10.25	5.20
Magnesia	0.71	0.69	
Lime	trace	0.27	0.25
Water at 100°	4.13	4.73	5.09
Water and organic matter, by ignition	7.50	5.45	4.22
	99.73	100.05	100.37

This analysis verifies the unusual purity of the specimen from Rappahannock, which was first observed.

THE PROTEOSE OF WHEAT.

BY THOMAS B. OSBORNE.

In this JOURNAL, Vol. 19, page 65, in a paper on "Alcohol Soluble Proteid of Wheat," Mr. G. E. Teller, after stating that he had found in saline extracts of wheat flours, considerable quantities of the proteid gliadin, says: "Apparently it was this body which was found by Osborne and Voorhees in their salt solution extracts and was designated by them as a proteose and proteose-like body under captions V and VI."

Mr. Teller has assumed without reason that gliadin, as described by me and Mr. Voorhees, is *wholly* insoluble in 1 to 10 per cent. sodium chloride solutions and also that proteoses of wheat are completely precipitated by adding alcohol to 75 per cent. Both of these assumptions are unfounded, and therefore it is not surprising that he obtained reactions for both gliadin and proteose in the 74 per cent. alcohol solution which he expected would contain only gliadin. Furthermore, as he points out, many of the reactions of gliadin are very likely those given in text-books for proteoses, but in our investigation of this seed, we were not misled by this fact, for we expressly called attention, page 404, Vol. 15, to differences

which we found between gliadin and the proteose there described.

Mr. Teller has overlooked the fact that we separated the proteids from our extract by saturating with ammonium sulphate, a process which rendered the gliadin insoluble in the strong saline solution in which the other proteids were subsequently redissolved.

In extracts made with salt solutions from which the proteids were separated without previous precipitation with ammonium sulphate, we found gliadin and recognized its presence without difficulty. Further, the proteose which we described, we separated as such from the extracts, and could therefore by no possibility have mistaken gliadin for it.

LABORATORY OF THE CONNECTICUT
AGRICULTURAL EXPERIMENT STATION.

REVIEWS.

AN INTRODUCTORY COURSE OF QUANTITATIVE CHEMICAL ANALYSIS, WITH EXPLANATORY NOTES AND STOICHIOMETRICAL PROBLEMS. BY HENRY P. TALBOT, PH.D., Associate Professor of Analytical Chemistry in the Massachusetts Institute of Technology. New York: The Macmillan Co. 1897.

At the sight of a new manual of chemical analysis one involuntarily exclaims "were there not already enough?" It may be said of most handbooks of qualitative and quantitative analysis that they simply embody the author's method of teaching the subject, and serve mainly the purpose of aiding him in the instruction of his own classes. Teachers have now-a-days come to attach great importance to methods and sequence in teaching, and are perhaps too apt to overlook the fact that success is less due to methods than to the direct impulse and inspiration which they give to their pupils through their personal influence.

But we find in Professor Talbot's Introductory Course to Quantitative Chemical Analysis something more than a book for local use. There is an idea running through it that is more or less new in books of this kind, and one which instructors will heartily welcome. The earnest and thorough teacher cannot see without regret his laboratory classes grow in size beyond his ability to deal with each student individually, and he tries to discover some means whereby he can manifold himself. This may in some degree be accomplished by additional instructors, but they bring inevitably a disturbing element into personal instruction. In Professor Talbot's book

there is an attempt to give the student not only the important and essential things which he should know in special cases, but what is of more importance so to direct his thoughts toward his work that he shall grasp the fundamental ideas governing chemical analysis. In other words, the directions and explanations are such as the thoughtful and conscientious teacher would give to his pupil in the laboratory in endeavoring to make him think intelligently for himself.

For example, in the section describing the method for the gravimetric determination of iron there is first given the "procedure" or minute directions for the successful precipitation from a solution of ferrous ammonium sulphate of ferric hydrate, and the subsequent ignition of the precipitate. Then follow eight "notes" giving the reasons for the different steps and the precautions which must be observed in order to secure accuracy of result. It is these notes which give the greatest value to the book, since they direct the student's attention to the great number of variables concerned, even in the simplest chemical analysis. It is safe to say that when a student has performed a few analytical processes under guidance as thoughtful and thorough as this, he will become not merely an accurate worker, but what is of infinitely more importance, a clear thinker and close observer.

The stoichiometrical problems are well chosen and will prove helpful to many a busy teacher. T. M. D.

A SIMPLE METHOD OF WATER ANALYSIS, ESPECIALLY DESIGNED FOR THE USE OF MEDICAL OFFICERS OF HEALTH. BY JOHN C. THRESH, M.D. (Vic.), D.Sc., (Lond.), D.P.H., (Camb.) 1897. London: J. & A. Churchill.

This little book explains a method for the chemical examination of water, as respects its fitness for ordinary domestic use, which has been worked out with a good deal of ingenuity, so as to avoid for the analyst multiplied weighings or the preparation of the volumetric solutions generally employed. It is proposed to accomplish this result by the use of "soloids"—evidently similar to the "compressed tablets" so much used for hypodermic medication in this country—each of which contains a definite, very small amount of a particular reagent, and "capsules," each containing in like manner a definite, small amount of the Nessler test solution. Under pressure as to time, or when deprived of the resources of a regularly equipped laboratory, the analyst would no doubt find these "soloids" and "capsules" convenient, though it may well be doubted whether some of those mentioned could be depended upon to keep without alteration for any considerable time. There is risk that the results of a "cut and

dried" system of water analysis may have undue weight attached to them, or, on the other hand, that such an analysis may come to be regarded too much as a proper form to be gone through with, though leading to no particular practical conclusions. It is only fair, however, to say that the author of this little work in his introduction points out the superior importance of submitting the source of a water to sanitary inspection rather than merely analyzing the water itself, and elsewhere suggests the chief use of the latter proceeding as indicating the degree of need for the former. J. W. M.

THE GASES OF THE ATMOSPHERE. THE HISTORY OF THEIR DISCOVERY. BY WILLIAM RAMSAY, F.R.S., Professor of Chemistry in University College, London. Macmillan & Co. 1896.

Professor Ramsay describes his book as one written for those who are "without any special scientific training." There is no doubt, however, that chemists will be as ready as others to acknowledge their debt to one who has brought together, in a book of convenient size, the principal facts connected with the history of scientific research upon the composition and properties of the atmosphere.

The book may be divided into two parts, in the first of which are described the discovery of the complex nature of the atmosphere and the isolation of the various constituents, whose presence was recognized prior to 1894. The author starts out by discussing the three principal causes for the tardy recognition of the nature of the air, *viz.*, (1) the confusion of gases with one another; (2) erroneous ideas regarding the phenomena of combustion; and (3) the lack of attention to changes in weight accompanying chemical action. These points are then illustrated in the erroneous conclusions so frequently drawn from their experiments by even such brilliant thinkers as Boyle and Mayow, Black and Priestley, Scheele and Cavendish. Looking back in the light of modern knowledge, one is tempted to underestimate the real genius of the experimenter in view of the unproved and frequently illogical position he was led to assume. As Professor Fitzgerald has recently said of certain other scientific deductions "they are almost taken for granted as a natural possession of the human mind. We are inclined rather to think our predecessors must have been blind not to see such obvious things than to credit the discoverers with preternatural insight."

The author takes up in order the conjectures of Boyle, built as they were in large measure upon the metaphysical reasoning of the Schoolmen; the extraordinary insight of Mayow into the true nature of the process of oxidation—a thoughtful, original investigator, a full century before his

time—and the experimental results of Hales, which did not, nevertheless, entirely free his mind from the notion of the identity of all gases. The development of the theory of phlogiston by Stahl is followed by accounts of the discovery of carbon dioxide by Black, and of nitrogen by Rutherford. Next is a chapter upon the discovery of oxygen by Scheele and Priestley and the overthrow of the phlogiston theory through the researches of Lavoisier. Finally, the first part of the book closes with an account of the researches of Cavendish—among others, the discovery of the composition of water and the analysis of the air.

The second part enumerates the facts which led to the discovery and isolation of argon, gives in detail the properties of that gas, and discusses the relation of the substance to the general system of the elements. In the course of these chapters Professor Ramsay disposes very completely of the notions that argon is an allotropic form of nitrogen, and that it is a mixture. He also finds no evidence in favor of the existence in the gas of molecules of different degrees of complexity. A possible explanation of the fact that the atomic weight of the gas is apparently about two units higher than that corresponding to its probable position in the system, is then given. It may be stated thus: The "atomic weight" of an element capable of forming compounds is, as we know it, not necessarily a true measure of its atomic mass, but is the resultant of the several forces acting upon the atom while in combination. Chief perhaps among these is the attraction of gravitation, but this does not act alone: intramolecular forces tend to decrease its effect. Hence the true atomic weight of such an element is possibly somewhat greater than the weight we measure; the difference between the two varies somewhat in individual cases, and, therefore, the differences between the atomic weights as determined for the elements in a given group vary irregularly about a mean value approximately 16 in the first three series. On the other hand, in the case of elements like argon and helium, apparently incapable of forming compounds, the determined atomic weight may be a true measure of the atomic mass, since intramolecular forces have no existence.

Finally, it may be said the book is well abreast of the times. It is eminently readable and its interest is heightened by the introduction of a number of portraits. W. W. R.

A MANUAL OF QUANTITATIVE CHEMICAL ANALYSIS FOR THE USE OF STUDENTS. BY FREDERICK A. CAIRNS, A.M. Third Edition. Revised and enlarged by Elwyn Waller, Ph.D. 8vo. 417 pp. New York: Henry Holt & Co. 1896. Price \$2.00.

The manual is designed "to assist beginners in the prac-

tice of quantitative analytical chemistry," and to serve at the same time, as a reference book for more advanced analytical chemists. The first twenty pages are devoted to such detailed suggestions bearing upon the operations of quantitative analysis in general, as are likely to prove helpful to the beginner; these are followed by nine typical analyses of simple bodies, and these, in turn, by directions for the analyses of thirty more complex substances, including minerals, ores and industrial products, comprehending, in all, a considerable variety of determinations. The present (third) edition has been enlarged to 417 pages (the first edition contained 270 pages). A number of the chapters have been re-written and expanded, and chapters relating to the analysis of chromite, aluminum bronze, and commercial nitrates have been added, while the chapters relating to the analysis of superphosphates and acetates of lime, guano, raw and refined sugar, flour, milk, turpentine, soap, and petroleum, which are found in the earlier edition, have been omitted from this later one. Still other chapters of the earlier edition are unaltered, or are changed only by the addition of a note at the close.

About forty pages of the material treating of the "Properties of Precipitates, etc.," written by the editor, have been added to the appendix in this edition. This material, the author states, is intended to serve as a substitute for the subject matter included under "Forms" in Fresenius' Quantitative Analysis, and to have the advantage over the latter, of greater convenience for reference. The classification of properties adopted to accomplish this end does not seem to be altogether fortunate, and the statements of many of the properties, as given, are inexact, and would sometimes be misleading to the beginner. By a more complete compilation of recently published data to supplement those given by the older authority, and greater care with respect to accuracy of statement, the author would have imparted to his work a far greater value.

The wide range of analyses presented offers a liberal course of instruction in inorganic quantitative analysis, and the procedures have, with few exceptions, if any, been wisely selected for that purpose. The same tendency toward inexactness already noted is occasionally evident through the book, and the diction is not always as smooth as might be desired. It is doubtful if the work is sufficiently comprehensive and authoritative to satisfy the needs of the analytical chemist in active practice, as a reference book. H. P. T.

OBITUARY NOTE.

EUGEN BAUMANN.

Eugen Baumann, the distinguished professor of chemistry in the medical faculty of the University of Freiburg, Germany, died Nov. 30, at the age of 50. Baumann began his career as an apothecary, but soon entered the University of Tübingen, and took up work under the direction of Hoppe-Seyler, who was then professor of physiological chemistry there. In 1872, when Hoppe-Seyler was called to Strasbourg, Baumann went with him as his first assistant. In 1877 Baumann was called to Berlin to take charge of the chemical division of the Physiological Institute. Here he remained until 1883, when he went to Freiburg as the successor of Von Babo, and there he remained until his death.

Baumann's work has been, for the most part, in the field of physiological chemistry, although he has also been active in pure chemistry, though, even in this field, the problems that specially interested him were such as had a direct bearing upon physiology. His last important contribution was the discovery that iodine is a never-failing constituent of the thyroid gland, that it is present in the gland in the form of an organic compound, and that this substance containing iodine is the "active principle" of the preparations made from the gland, and used in medicine.

In the course of his studies of cystin he took up the investigation of the mercaptals and mercaptols, and thus he was led to the discovery of the well-known compounds, sulphonal and trional, which have proved of such great value in medicine. Among the many problems upon which he has worked with marked success, the following may be mentioned: The complex sulphuric acids in urine; the transformations of aromatic compounds in the animal organism; the active condition of oxygen; the presence of glucose in normal urine.

I. R.
